

Regulating Intrinsic Electronic Structures of Transition-Metal-Based Catalysts and the Potential Applications for Electrocatalytic Water Splitting

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Abstract: Efficient and low-cost transition metal (TM)-based electrocatalysts have been of great importance to produce hydrogen (H₂) and oxygen (O₂) via electrocatalytic water (H₂O) splitting to ameliorate global energy and environmental problems. However, TM-based materials generally suffer from unsatisfactory electrocatalytic activity because of their relatively low conductivity and unregulated electronic structure. Therefore, electronic structure engineering on electrocatalysts is an efficient strategic approach to enhance catalytic performances and stabilities. In this review, recent experimental and theoretical advances on intrinsic electronic structure regulation of TM-based nanomaterials are summarized in terms of preparation methods and underlying natures to boost hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Systematic discussion is conducted on engineering strategies for TM-based nanomaterials to regulate their electronic structures, optimize their adsorption ability of reaction intermediates, and reduce the reaction energy barrier. The existent challenges and perspectives of TM-based electrocatalysts are highlighted to provide new insights into technological advancement for hydrogen production.

1. Introduction

The increasing demands for renewable clean energy resources and concerns of global environmental issues have attracted lots of interests in developing energy conversion and storage technologies. Among these approaches, efficient water decomposition with negligible environment pollution powered by electricity (Figure 1a) is an interesting method to produce clean hydrogen fuels,¹⁻³ which consists OER at the anode and HER at the cathode (shown in Figure 1b). Both of them involve multistep proton-coupled

electron transfer that is intrinsically efficiency-limited for water electrolysis.^{4,5} Highly effective catalysts are always required to accelerate the catalysis rate, enhance the conversion efficiency, and reduce the overpotential of water dissociation. Until now, the most effective materials for catalyzing OER are IrO₂ and RuO₂, and the benchmark catalysts for HER are Pt group metals. However, high cost, scarcity, and instability of noble metal-based electrocatalysts seriously restrict their large-scale applications. Hence, designing and synthesizing cost-effective and efficient TM-based nanomaterials for large-scale water splitting have been an imperative yet challenging subject. Extensive efforts have been made to exploring high-efficiency OER and HER electrocatalysts based on TM elements, such as oxides, selenide, phosphides, and hydroxides for OER⁶⁻¹² and carbides, chalcogenides, nitrides, and alloys for HER.¹³⁻¹⁸ Unfortunately, most transition metal (TM)-based catalysts have inadequate intrinsic activities compared with noble metal materials because of their relatively low conductivity and unsuitable electron structure. Electrocatalysis is always operated in harsh conditions (acidic or alkaline electrolyte) to minimize the overpotentials of water splitting. This harsh electrolyte condition poses a great challenge for most TM-based materials applied as a highly active and stable catalyst during practical application. These aspects have encouraged various engineering strategies for TM-based electrocatalysts to enhance oxygen and hydrogen evolution activity and stability.

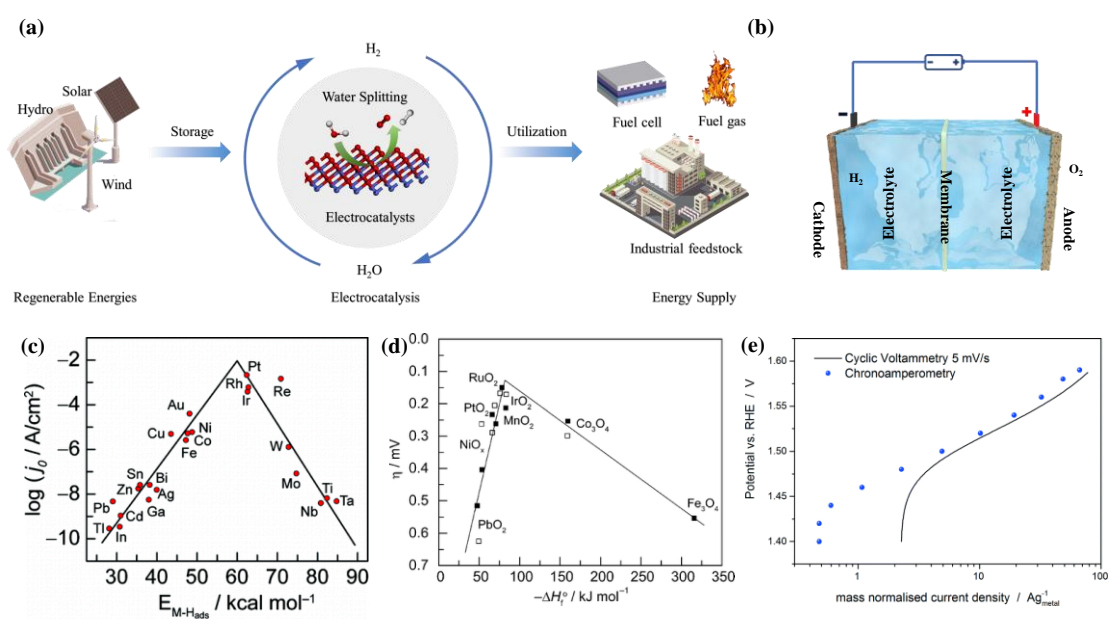


Figure 1. (a) The production and utilization cycle of H₂. (b) Schematic illustration of water electrolyzer. (c) Volcano plot of different HER metal-based electrocatalysts in acidic solution. (d) Volcano plot of OER overpotential vs. enthalpy of different metal oxides in acidic (■) and basic (□) solutions. Reproduced with permission.¹⁹ Copyright 2010, American Chemical Society. (e) Tafel curves obtained from cyclic voltammetry measurement and chronoamperometry test in 0.1 M HClO₄ solution using IrTiO₂ as electrode. Reproduced with permission.³⁰ Copyright 2014, Royal Society of Chemistry.

Herein, we summarized the reported engineering strategies for TM-based water splitting electrocatalysts, including support effects, interface effects, crystal faces tuning, elemental doping, defects tuning, and some other strategies. To validate the versatility of each mentioned strategy, various common electrocatalysts for HER (TM-based carbides, alloys, sulfides, and nitrides) and OER (TM-based oxide, selenides, and phosphides) were referred to as examples for discussion. Moreover, how each strategy tunes the electrocatalysts to enhance the catalytic performances is also carefully illustrated in the following sections. This research review aims to: i) improve the conductivity and boost the electron transfer from catalysts to reactant species; ii) increase the active sites and engineer the active centers of TM-based catalysts to enhance the intrinsic activities; iii) tune the electronic structures of TM-based catalysts and optimize the adsorption abilities of intermediate species via feasible strategies to lower reaction barriers. By presenting reported results, current challenges, and opportunities, we hope that our work could be of assistance in designing and engineering cost-effective TM-based electrocatalysts for water splitting.

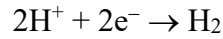
2. Electrochemistry of water splitting

2.1. Hydrogen evolution reaction

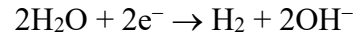
In general, a water splitting electrolyzer is consisted by cathod, membrane, anode and electrolyte, in which hydrogen evolution catalysts are coated on the cathode, and

H₂O are decomposed into H₂ at the surface of catalysts under a certain voltage. According to different electrolytes in which water splitting occurs, H₂ can be produced via different steps.

Acidic electrolyte:



Neutral or alkaline electrolyte:



HER involves three possible reaction steps. In acidic electrolyte, the first process is Volmer step ($\text{H}^+ + \text{e}^- \rightarrow \text{H}_{\text{ads}}$) to generate adsorbed hydrogen atom (H_{ads}) through the reaction of an electron with proton over the electrode surface. After the generation of H_{ads} species, H₂ production proceeds through the Tafel step ($\text{H}_{\text{ads}} + \text{H}_{\text{ads}} \rightarrow \text{H}_2$), the Heyrovsky step ($\text{H}_{\text{ads}} + \text{H}^+ + \text{e}^- \rightarrow \text{H}_2$), or both. In neutral or alkaline solution, the HER mechanism is still ambiguous, and the most accepted elementary reactions are Volmer step ($\text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}_{\text{ads}} + \text{OH}^-$), Heyrovsky step ($\text{H}_{\text{ads}} + \text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}_2 + \text{OH}^-$), and Tafel step. Hydrogen generation can proceed via Volmer–Heyrovsky, Volmer–Tafel, or Volmer–Heyrovsky/Tafel path. Regardless of the reaction routes, the H_{ads} species play an important role in HER, so its free energy (ΔG_{H^*}) could be an important descriptor for hydrogen-evolving catalysts. Optimal HER catalysts should possess a nearly zero ΔG_{H^*} to balance the adsorption and desorption of H and H₂. A volcano plot of different metal-based HER electrocatalysts (Figure 1c) has been summarized based on the exchange current density (j_0) and the M-H bond energies; this curve permits a comparison of catalytic performances and serves as a guide in developing highly effective metal-based electrocatalysts.¹⁹ Therefore, volcano plots drawn based on reliable HER data of various electrocatalysts are valuable for researchers.

2.2. Oxygen evolution reaction

Oxygen evolution catalysts are utilized at the anode in water splitting electrolyzer, and oxygen gases are subsequently produced when an external potential is applied.

Nevertheless, the OER at anode is more complex than the HER because of its four-electron oxidation processes. The large overpotential of OER mainly restricts the development and application of water splitting. Hence, OER-related research has been intensively performed to develop optimal catalysts that can greatly minimize the overpotential of water electrolysis. Exploring the catalytic mechanism of OER is also important in designing advanced electrocatalysts. In general, the reaction mechanism changes when different pH electrolytes are employed (see below).

Acidic or neutral electrolyte:



Alkaline electrolyte:

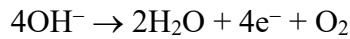


Table 1. Possible elementary reaction steps of OER over oxides in both acid and alkaline aqueous solution.

Acid Solution	Alkaline Solution
<p>(1) Electrochemical oxide path^{20,21}</p> <p>* + H₂O → *-OH + H⁺ + e⁻</p> <p>*-OH → *-O + H⁺ + e⁻</p> <p>2*-O → 2* + O₂</p>	<p>(1) Electrochemical oxide path^{20,21}</p> <p>* + OH⁻ → *-OH + e⁻</p> <p>*-OH + OH⁻ → *-O + H₂O + e⁻</p> <p>2*-O → 2* + O₂</p>
<p>(2) Oxide path²¹</p> <p>* + H₂O → *-OH + H⁺ + e⁻</p> <p>2*-OH → *-O + * + H₂O</p> <p>2*-O → 2* + O₂</p>	<p>(2) Oxide path²¹</p> <p>* + OH⁻ → *-OH + e⁻</p> <p>2*-OH → *-O + * + H₂O</p> <p>2*-O → 2* + O₂</p>
<p>(3) Krasil'shchikov path²²</p> <p>* + H₂O → *-OH + H⁺ + e⁻</p> <p>*-OH → *-O⁻ + H⁺</p> <p>*-O⁻ → *-O + e⁻</p> <p>2*-O → 2* + O₂</p>	<p>(3) Krasil'shchikov path²²</p> <p>* + OH⁻ → *-OH + e⁻</p> <p>*-OH + OH⁻ → *-O⁻ + H₂O</p> <p>*-O⁻ → *-O + e⁻</p> <p>2*-O → 2* + O₂</p>
<p>(4) Wade and Hackerman's path²³</p> <p>2* + 2H₂O → *O + *H₂O + 2H⁺ + 2e⁻</p> <p>*O + 2*OH⁻ → 2* + *H₂O + O₂ + 2e⁻</p>	<p>(4) Yeager's path^{24,25}</p> <p>* + OH⁻ → *-OH + e⁻</p> <p>*^z-OH → *^{z+1}-OH + e⁻</p> <p>2*^{z+1}-OH + 2OH⁻ → 2* + 2H₂O + O₂</p>

The possible elementary reaction steps of OER under alkaline or acidic solution conditions are summarized in Table 1, where M represents an active site on catalyst surfaces. In an acidic solution, the electrochemical oxide path has been the most accepted reaction mechanism, where H₂O adsorption and dissociation is the first and crucial step. Thus, regulating H₂O adsorption on electrocatalysts in acidic media can boost OER performances. Under alkaline condition, the OH⁻ adsorption on the active site is the first step, followed by different intermediate reaction steps. Among the elementary reaction steps of OER, the rate-determining step with highest reaction barrier could indicate the overpotential of the whole reaction. For ideal catalysts, the free energies of each elemental step should be similar and close to 1.23 V. Figure 1d exhibits the volcano plot of the OER overpotentials of TM oxide materials versus their transition enthalpy.¹⁹ Obviously, RuO₂ and IrO₂ are positioned at the top due to intrinsic good conductivity as well as advisable electronic structures. Therefore, feasible engineering strategies can be developed for low-cost TM-based materials as promising candidates with noble metal catalyst-like properties for water splitting.

2.3. Evaluation of electrocatalysts

2.3.1. Overpotential (η) and current density (j) at certain potentials

For both HER and OER, extra potentials larger than theoretical potential is required to trigger reactions, which is called as overpotential (η).²⁶⁻²⁸ The overpotential includes three categories, namely, activation, concentration, and that caused by the uncompensated resistance in the electrochemical interfaces for HER and OER. Activation overpotential has been the key parameter to evaluate catalysts, because it has the most important contribution to total overpotential. Concentration overpotential is generated from the sudden concentration drop of reactants and which could be minimized via stirring. While ohmic drop compensation can be used to optimize the resistance overpotential. The overpotential for HER and OER can be obtained from the

polarization curve tested by linear sweep voltammetry (LSV). Moreover, the current density (j) at high potentials based on LSV is another alternate activity parameter, especially for practical utilizations.

2.3.2. Tafel slope and exchange current density (j_0)

The Tafel plot can generally be derived from the LSV curve, where the slope values can be obtained using Tafel equation:²⁹

$$\eta = a + b \log(j)$$

In this equation, b is the Tafel slope value, which suggests charge transfer abilities of an electrocatalyst. Therefore, the Tafel slope can describe the mechanism of electrode reactions. When η is set to 0, the obtained j is defined as exchange current density (j_0), which is often used to illustrate intrinsic activities of electrocatalysts. Owing to capacitive currents, scan rate greatly influences the LSV used for Tafel plot, thus possibly leading to errors in determining the Tafel slope and j_0 to some extent. Therefore, the steady state currents from $i-t$ curves under various potentials should be used to accurately calculate the Tafel slope and j_0 . A close comparison of Tafel slopes acquired by using j from CV and from chronoamperometric $i-t$ curves for commercial IrTiO₂ catalyst is provided in Figure 1e.³⁰

2.3.3. Long-term stability

The long-term stabilities of prepared materials are crucial indicators for their practical utilization and is usually evaluated by cyclic voltammetry (CV) accelerated degradation test at high scan rate, chronoamperometric, or chronopotentiometric approaches. The increase of onset potential or overpotential before and after CV tests indicates their stabilities. The smaller increase indicates a higher long-term stability. For chronoamperometry or chronopotentiometry testing, a fixed potential or current should be set to monitor the durabilities of catalysts.

2.3.4. Turnover frequency (TOF)

The TOF at certain overpotential is another instructive indicator for estimating the

catalytical activity of obtained electrocatalysts for HER and OER. TOF can generally be calculated by the number of moles of products generated per catalytic site per unit time. The TOF can exhibit the intrinsic activity of each catalytic site in the catalysts, but obtaining a precise TOF value is not easy due to difficulty in calculating the total catalytic sites of catalysts. A reasonable method to acquire TOF is to consider the surface atoms or the easily accessible atoms of the catalysts. The other TOF values are calculated by using an approach based on the total catalytic species in the catalysts.³¹⁻³⁴ TOF can provide useful insights on the comparative electrocatalytic performances of different catalysts when reasonable calculation is executed.

2.3.5. Faradaic efficiency (FE)

FE is a quantitative parameter applied to describe efficiencies of electron transfer from external circuit to desired products in the reaction system. For HER and OER, FE is defined as the ratio between quantity of H₂ or O₂ gas produced during the reaction and theoretical gas amount calculated from chronoamperometric or chronopotentiometric analysis.³⁵⁻³⁷

2.4. Design principles of electrocatalysts

HER and OER occur at the solid–liquid–gas interface with solid materials as electrocatalysts, liquid acid or alkaline aqueous solution as electrolytes, and H₂ or O₂ gas as the product. Primarily, the reactant (H⁺, OH⁻, or H₂O) is first adsorbed onto the catalyst surfaces. When a potential is applied, the electrons pass through catalysts to the interface, and an electrode reaction is then triggered to produce H₂ or O₂ gas. Finally, the gas products are released from the catalyst surface. Therefore, ideal catalysts should possess good chemical stability in acid or alkali electrolytes and under high potential conditions to achieve a good long-term working life. Given that HER and OER involve electron transfer through the catalysts, optimized catalysts should possess excellent electrical conductivity to facilitate electron transfer and effectively enhance the reaction rate. In addition, the proper abilities of reactant adsorption and product desorption are indispensable for good electrocatalysts. The binding abilities of multiple intermediates

of HER or OER over catalyst surfaces are also crucial, because when the binding energies are extremely high, the catalyst activity will be limited by the poisoning effect; however, when the species weakly bind to the active sites, activation over the electrocatalyst becomes difficult. Therefore, the proper binding energies of involved species are essential for the electrocatalysts and dramatically contribute to the catalytic performances. Moreover, low cost and environmental hazardless are also crucial requirements for objective electrocatalysts in large-scale water electrolysis.



Figure 2. Review scheme of design strategies, characterization, and theoretical analysis of high-performance TM-based electrocatalysts for large-scale water splitting application.

The above discussions have prompted the designing of advanced novel materials as catalysts or the engineering of traditional catalysts by facile strategies to obtain greatly enhanced performances. The following sections highlight the engineering strategies applied for traditional electrocatalysts to boost their HER or OER activities for pure H₂ production (as shown in Figure 2).

3. Engineering TM-based Electrocatalysts

3.1. Engineering by support effects

Coupling highly conductive supports with active nanomaterials has always been regarded as a promising approach to enhance the conductivity. At the same time, the electronic structures of active materials can also be engineered via support effects, further significantly affecting the electrocatalytic activities. As a result, the enhanced conductivity of as-prepared catalysts could contribute to fast charge transfer from catalysts to interfaces of catalysts and reactant, leading to fast reaction dynamics. Moreover, the tuned electronic properties of electrocatalysts can optimize the bonding capacities of intermediates over electrocatalysts during HER and OER, significantly reducing the reaction barriers. Therefore, various supports have been employed to enhance electrocatalytic performances of TM-based nanomaterials.³⁸⁻⁴⁰ Particularly, carbon-based supports with high specific surface area and metal-based supports with good electrical conductivity were widely investigated in HER and OER.

3.1.1. Carbon-based support effects

Owing to good electrical conductivity, high specific surface area and easy modifiability, various carbon-based nanomaterials (such as graphene, heterogeneous atom doped porous carbon), have been employed to support active catalysts to boost their electron conductivity and tune the electronic structures, recently.⁴¹⁻⁴³ For instance, Lan's group synthesized a novel HER composite electrocatalyst containing molybdenum carbide and reduced graphene oxide (denoted as Mo₂C@NPC/NPRGO) through the pyrolysis of ternary polyoxometalate-polypyrrole/RGO precursor at 900 °C (Figure 3a).⁴⁴ The SEM and TEM images of as-obtained Mo₂C@NPC/NPRGO catalyst indicated that its morphology is similar to that of original precursors, and the Mo₂C possessing an average size of 2–5 nm was anchored on RGO surface at a high density. Clear lattice fringes of Mo₂C@NPC/NPRGO showed an interplanar distance of 0.238 nm in HRTEM image, suggesting the explored (111) planes of Mo₂C nanoparticles (NPs). In addition, the Mo₂C NPs are enveloped by carbon layers, preventing the aggregation of Mo₂C NPs as well as enhancing their stability during catalysis. As shown

in Figure 3b. the as-prepared Mo₂C@NPC/NPRGO electrocatalysts exhibited excellent HER activities with a low onset overpotential of 0 mV. Moreover, the overpotential to reach current density of 10 mA cm⁻² (denoted as η_{10}) of Mo₂C@NPC/NPRGO catalyst was low as 34 mV, much better than that of Mo₂C@NPC. The Tafel slope value of Mo₂C@NPC/NPRGO (Figure 3c) is approximately 33.6 mV/dec, which is superior to that of Mo₂C@NPC, confirming the roles of NPRGO support in boosting HER performances. Density functional theory (DFT) results in Figure 3d revealed that the Mo₂C@C-graphitic N possess the lowest ΔG_{H^*} value of 0.69 eV, verifying that the carbon support is important in tuning H bonding energy. Besides, Peng and co-workers synthesized Mo₂C/N-PC with nitrogen-doped porous carbon as the supporter. The prepared Mo₂C/N-PC catalyst showed excellent HER activities in 0–14 pH range. DFT calculations demonstrated that support effect can contribute to a decreased ΔG_{H^*} .⁴⁵ These experimental and theoretical results certified that the support effects of carbon-based materials could efficiently boost HER activities by engineering the conductivity and electronic structures of catalysts. In addition, alloy FeCo NPs completely encapsulated in carbon (with a thickness of approximately 1.71 nm) were successfully prepared via pyrolysis of metal–organic frameworks.⁴⁶ Due to the support effect, as-prepared catalyst exhibited enhanced catalytic HER activities. DFT calculations indicated that the electronic structures of composite catalysts was regulated through carbon layer support effect. Similarly, RuCo anchored on N-doped porous carbon nanomaterials were also synthesized via a method of annealing Prussian blue analogs under N₂ atmosphere as illustrated in Figure 3e.⁴⁷ These RuCo/NC catalysts consist of abundant alloy RuCo NPs (about 30 nm) coated with carbon (from 1 to 15 layers). Calculated charge-density difference of Co₃Ru model (Figure 3f) confirms that the transfer of electrons from metals to graphene supports is beneficial in lowering the ΔG_{H^*} . As HER catalysts, the RuCo/NC with Ru content of 3.58 wt.% (denoted as S-4) displayed a η_{10} of 28 mV (Figure 3g) in 1 M KOH aqueous media, which is superior to that of Pt/C. Furthermore, Tafel slope (Figure 3h) of S-4 sample is 31 mV dec⁻¹, closed to that of Pt/C, which suggests a rapid HER rate and Tafel–Volmer mechanism for this

RuCo/NC catalyst. DFT calculations (Figure 3i) illustrated that the ΔG_{H^*} could be reduced by the combination of metal NPs and graphene. The Ru₃Co-N-doped graphene structure has a optimal ΔG_{H^*} value (0.31 eV), thus confirming the roles of carbon-based support in improving HER performances.

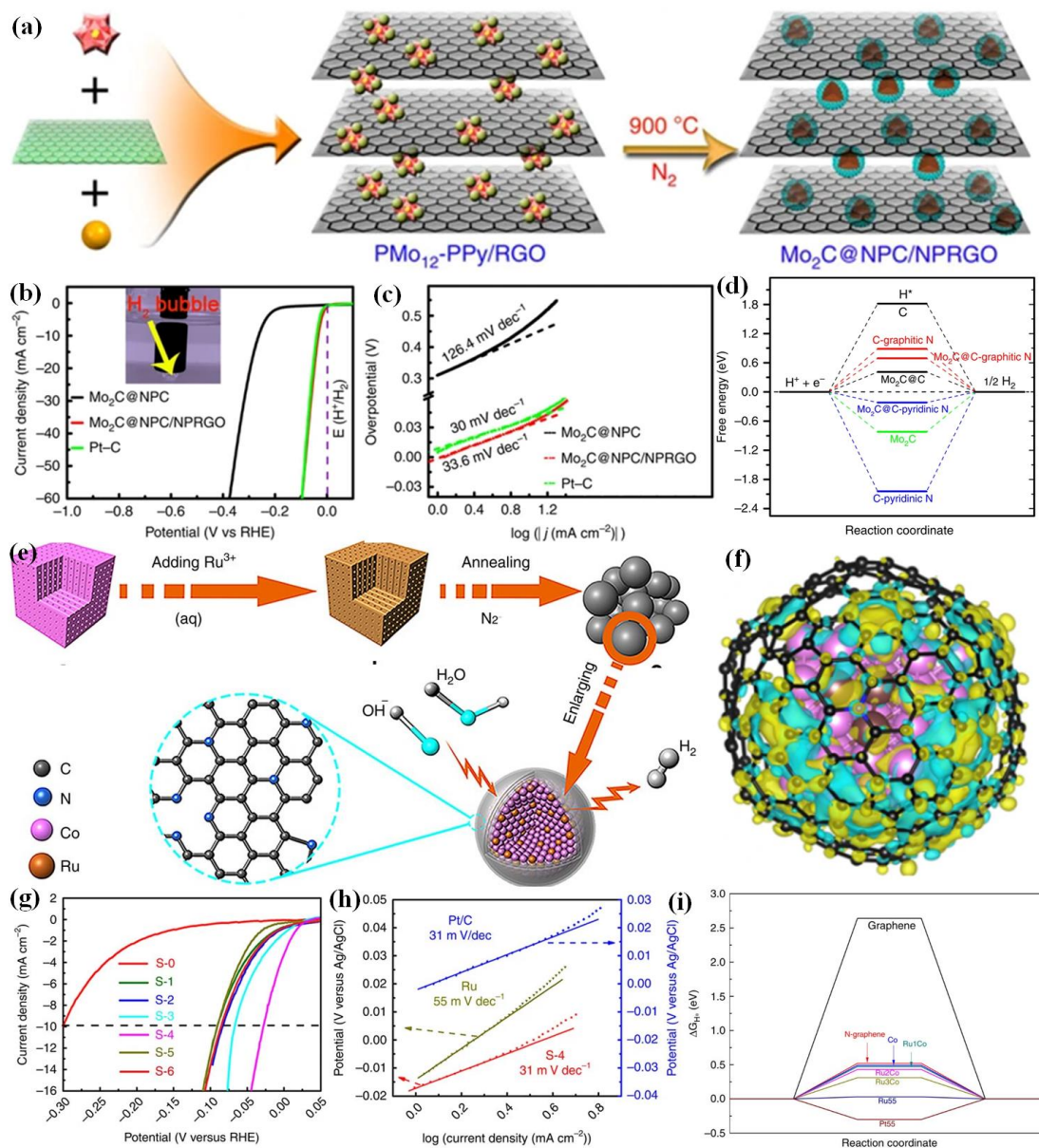


Figure 3. (a) Schematic illustration for synthesizing Mo₂C@NPC/NPRGO composite catalyst. (b) The LSV curves for HER and (c) Tafel plots of catalysts in 0.5 M H₂SO₄ electrolyte. Inset in (b): H₂ bubbles produced over the Mo₂C@NPC/NPRGO catalyst. (d) The ΔG_{H^*} of related catalysts. Reproduced with permission.⁴⁴ Copyright 2016, Nature Publishing Group. (e) The synthetic process of RuCo@NC as HER

electrocatalysts. (f) Calculated charge-density differences of Co_3Ru with color region isosurface value of $0.01 \text{ e } \text{\AA}^{-3}$. (g) LSV curves for HER of RuCo@NC samples in 1 M KOH solution. (h) Tafel slope plots of Pt/C, Ru and S-4 catalysts. (i) Calculated ΔG_{H^*} over different electrocatalysts. Reproduced with permission.⁴⁷ Copyright 2017, Nature Publishing Group.

OER is more kinetically sluggish than HER due to its multistep oxidation, and support effects can also work as a potential method to enhance OER performances by engineering conductivities and electronic structures of TM electrocatalysts. For example, Yu and co-workers reported NG- CoSe_2 catalyst containing CoSe_2 nanobelts and N-doped graphene oxides for OER in 0.1 M KOH solution.⁴⁸ Graphene possessing good electrical conductivity was selected as support to anchor CoSe_2 nanobelts. After hydrothermal reaction as shown in Figure 4a, flexible CoSe_2 nanobelts were tightly loaded on the NG surfaces. TEM image clearly illustrated that the ultra-long belt-like CoSe_2 was anchored on NG sheets, and the obtained nanobelts consisted of numerous CoSe_2 NPs. Moreover, the (211) plane of cubic CoSe_2 and graphene (001) plane were clearly observed in the catalyst. The as-prepared NG- CoSe_2 as OER electrocatalysts displayed smaller onset overpotential (0.293 V) and higher catalytic current than CoSe_2 nanobelt references (Figure 4b), as well as lower Tafel slope 40 mV/dec. These enhanced OER activities mainly originated from the support effects involving intimate connections between CoSe_2 and NG (Figure 4c and 4d). Li and co-workers reported CoSe_2 nanowires combined with nitrogen-doped carbon ($\text{CoSe}_2@\text{N-CNWs}$), which could act as a potential OER catalyst in 1.0 M KOH media. Due to the enhancement of electric conductivity, optimized free adsorption energy of OER intermediates, these $\text{CoSe}_2@\text{N-C}$ NWs exhibited an enhanced 6.61-fold catalytic activity than CoSe_2 NWs at η of 340 mV.⁴⁹ Additionally, $\text{Co}_3(\text{PO}_4)_2$ NPs coated by N-C were prepared by using bifunctional O-phospho-DL-serine reagent.⁵⁰ SEM and TEM images clearly showed the $\text{Co}_3(\text{PO}_4)_2$ NPs are approximately 100 nm. HRTEM revealed that $\text{Co}_3(\text{PO}_4)_2$ NPs were supported by N-doped carbon layers. In 1 M KOH media, the obtained $\text{Co}_3(\text{PO}_4)_2@\text{N-C}$ exhibited excellent performances toward OER with a small η_{10} of 317

mV and a low Tafel slope value of 62 mV dec^{-1} , which are superior to that of pure $\text{Co}_3(\text{PO}_4)_2$ catalyst. The excellent activities are benefitted from the abundant active sites of $\text{Co}_3(\text{PO}_4)_2$ NPs and high electrical conductivity caused by N doped carbon layers. FeOOH is also regarded as a promising catalyst for OER, but its intrinsic poor electron conductivity hinders catalyzing OER. Li's group presented depositing FeOOH particles onto ZIF-derived N-doped carbons (NPCs) as shown in Figure 4e could improve the electron conductivity and boost the catalytic performances.⁵¹ In alkaline media, this FeOOH/NPC catalyst exhibited a small η_{100} of 230 mV (Figure 4f) and a low Tafel slope of 33.8 mV dec^{-1} (Figure 4g), as well as good durability (Figure 4h). Besides, many TM-based electrocatalysts supported by carbon-based matrix have been reported, confirming that carbon-based support effects could efficiently enhance the catalytic activities via improving the conductivity and tuning the electronic structures.⁵²⁻⁶⁰

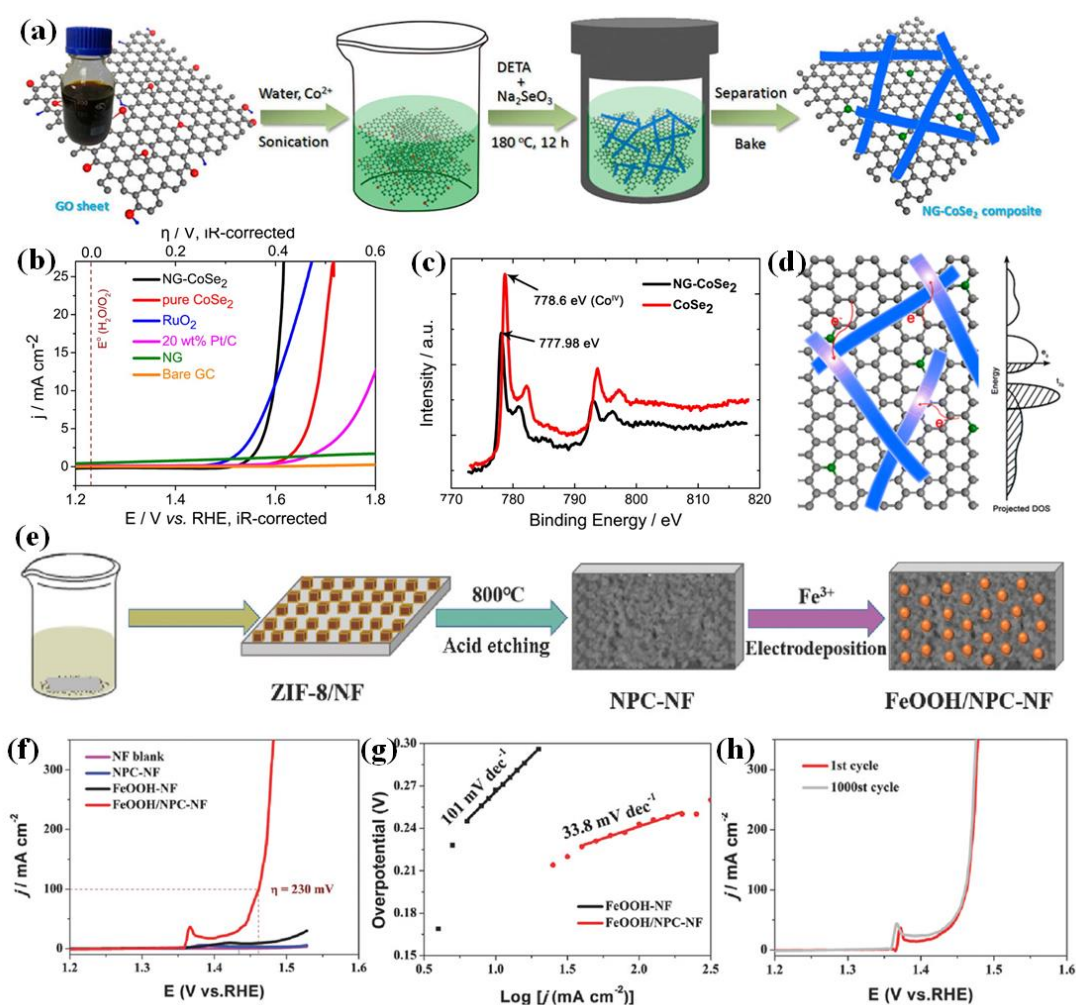


Figure 4. (a) Schematic illustration for constructing NG-CoSe₂ composite electrocatalyst. (b) The LSV curves towards OER of catalysts. (c) High-resolution XPS spectra of Co 2p. (d) The electron donation image of NG-CoSe₂ and the schematic DOS of CoSe₂. Reproduced with permission.⁴⁸ Copyright 2014, American Chemical Society. (e) The fabrication process of FeOOH/NPC-NF electrode. (f) The LSV curves for OER, and (g) related Tafel plots. (h) LSV curves for stability assessment. Reproduced with permission.⁵¹ Copyright 2018, Wiley-VCH.

3.1.2. Metal-based support effects

Metal-based supports possessing richer electrons and better conductivity than carbon have been widely employed as promising supports and mediators to engineer the activities of electrocatalysts. In 2014, Jen's group utilized periodic DFT with BEEF-vdW functional to explore HER performances on supported MoS₂ catalysts, including MoS₂, MoS₂-Au, and MoS₂-graphene three different systems.⁶¹ Compared to MoS₂, the ΔG_{H^*} values of MoS₂-Au and MoS₂-graphene have been increased by 0.56 and 0.18 eV. This work also revealed that support effects could greatly change the H binding energy, which contributes to several orders of magnitude improvement. In 2017, experimental results further confirmed the role of metal support effects on boosting electrocatalytic HER activities.⁶² [Mo₃S₁₃]²⁻ cluster anchored on Au, Ag, Cu, and GC supports were prepared, and [Mo₃S₁₃]²⁻ on Au support showed the smallest onset potential that was better than [Mo₃S₁₃]²⁻ on glassy carbon. Related DFT calculation proved that metal Au support can efficiently tune the ΔG_{H^*} of electrocatalysts for HER. For OER electrocatalysts, metal-based supports are usually employed to boost the catalytic performances by regulating electronic properties and improving conductivity. For instance, cobalt oxide films with a thickness of 0.4 monolayer were deposited onto various metal supports.⁶³ In 0.1 M KOH solution, cobalt oxide/Au sample displayed the most remarkable enhancement of anodic currents (Figure 5a), revealing that Au

support surely improves catalytic performances of cobalt oxide catalysts. Calculated TOF of cobalt oxide films on different metal supports showed that cobalt oxide/Au sample was 40 times better than pure cobalt oxide. Moreover, the catalytic OER performances of cobalt oxide supported by different metals increased with increasing electronegativity of metals ($\text{Co} < \text{Cu} < \text{Pd} < \text{Pt} < \text{Au}$). Experimental and theoretical results revealed that the increase in Co^{IV} cations in the supported cobalt oxides caused by metal-substrate is greatly attributed to these enhanced OER activities. In 2017, a self-supporting electrode consisted of Co_2P NPs anchored on Co foil was synthesized via the one-step phosphorization method (Figure. 5b).⁶⁴ The SEM image in Figure 5c shows that the Co_2P NPs were uniformly fixed on the surface of Co foil after phosphorization, thereby generating a continuous and porous film on the Co foil surfaces, which could greatly enlarge contact area of Co_2P NPs and electrolyte. The TEM image in Figure 5d of Co_2P displayed an irregular NP morphology, and the HRTEM image (Figure 5e) exhibited the clear lattice spacing of 0.22 nm, confirming the exposed (112) crystal plane of Co_2P . Figure 5f and 5g show the HER and OER performances of $\text{Co}_2\text{P}/\text{Co}$ -foil electrode and the Co_2P NPs peeled off from the integrated electrode. In 1 M KOH solution, the $\text{Co}_2\text{P}/\text{Co}$ -foil integrated electrode showed superior activities with η_{10} of 157 mV for HER and 319 mV for OER, respectively, which are better than those of pure Co_2P NPs. Finally, this integrated $\text{Co}_2\text{P}/\text{Co}$ -foil can work as bifunctional electrodes and exhibits excellent overall water splitting activities (Figure 5h). These results confirmed that the metal-based support effects hugely contribute to conductivities and electrocatalytic activities. Results mentioned above reveal that support effects could tremendously enhance the conductivity and significantly tune electronic structures of active materials, leading to optimized adsorption abilities, as well as reduced reaction barriers, further greatly boosting the electrocatalytic activities. Accordingly, engineering the electronic structures of TM-based active materials using support effects in electrocatalysts could be an effective method for boosting electrocatalytic water splitting.⁶⁵⁻⁷⁰

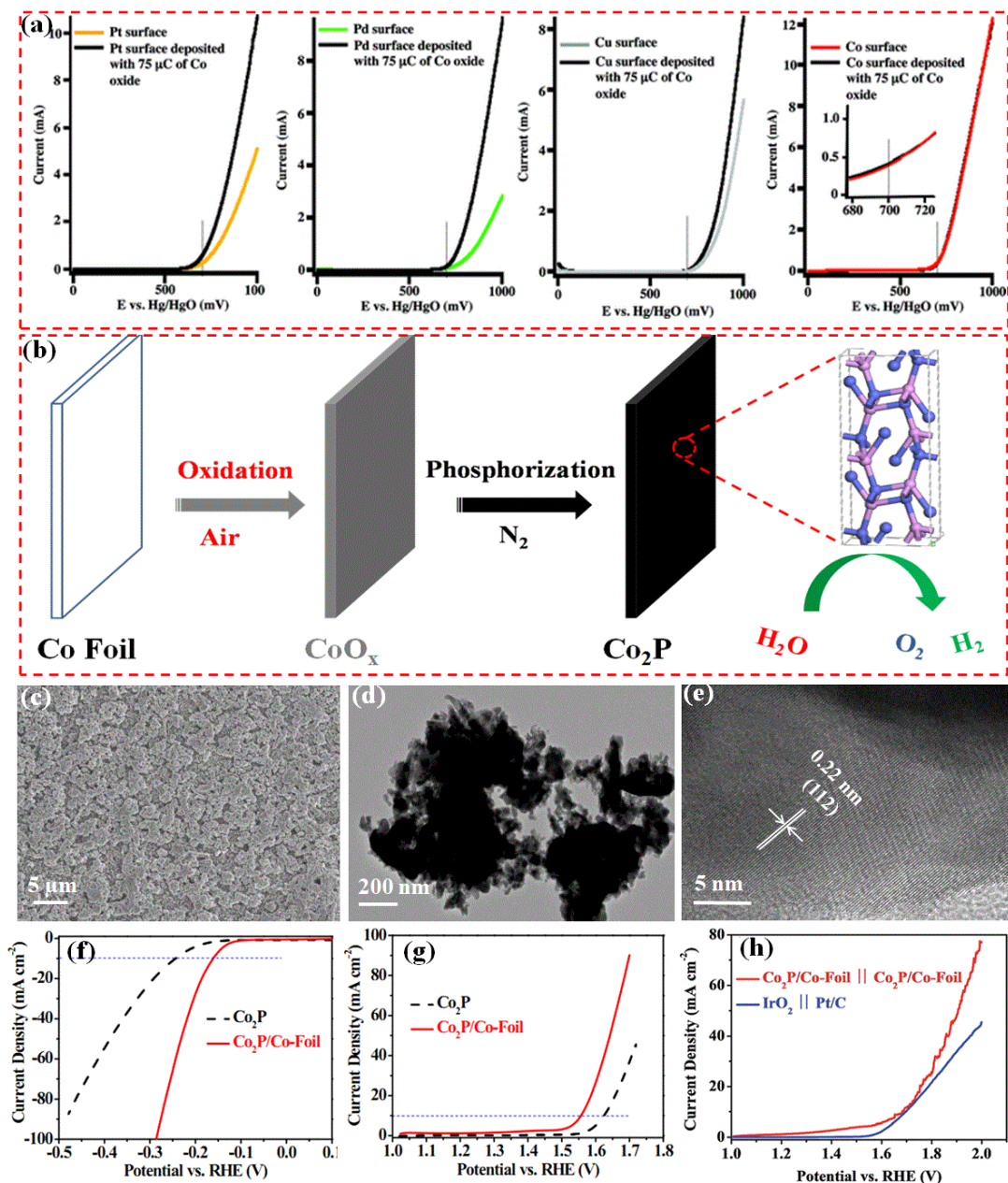


Figure 5. (a) The LSV curves of various metal electrodes with/without Co oxide in 0.1 M KOH, and dotted line marks 700 mV. Reproduced with permission.⁶³ Copyright 2011, American Chemical Society. (b) Schematic illustration for preparing Co₂P/Co-foil self-supporting bifunctional electrode. (c) The SEM, (d) TEM and (e) HRTEM images of Co₂P NPs. LSV curves for HER (f) and OER (g) of Co₂P particles and the integrated Co₂P/Co-Foil electrode. (h) LSV curves of Co₂P/Co-foil||Co₂P/Co-foil and IrO₂||Pt/C for water electrolysis in 1 M KOH solution. Reproduced with permission.⁶⁴ Copyright 2017, Royal Society of Chemistry.

3.2. Engineering by interface effects

Different from support effects, the interface effects generally equip the hybrid electrocatalysts with more active sites at the interfaces. Besides, the strong electronic interaction of different active materials can lead to higher combined catalytic performances than individual components.^{71,72} Moreover, abundant interfaces in the hybrid electrocatalysts bring diverse engineered electronic features that are favorable for optimizing their chemisorption abilities and further enhance their HER or OER kinetics.^{73,74} Therefore, engineering the catalysts using the strategy of interface effects is essential to boost catalytic activities and accelerate reaction kinetics via increasing the active sites and tuning electronic structures. For instance, Markovic's group prepared a Ni(OH)₂/Pt composite material that can be used as a HER electrocatalyst, which contains uniform Ni(OH)₂ clusters with height of 0.7 nm and size of 8–10 nm.⁷⁵ CV curves revealed that the Ni(OH)₂/Pt electrocatalyst displays better adsorption and irreversible reduction of OH_{ad} compared with pure Pt electrode because of the high oxophilicity of Ni(OH)₂ clusters. Consequently, the Ni(OH)₂/Pt hybrid material exhibited an eightfold increase in HER activity in 0.1 M KOH solution compared with Pt material, suggesting that the interface effects improves the catalytic HER performances. DFT calculations revealed that the forceful interaction of Ni(OH)₂ with O atoms and Pt with H atoms can synergistically enhanced the H₂O adsorption on the interfaces of Ni(OH)₂/Pt electrocatalyst. Moreover, the edges of Ni(OH)₂ clusters at the interfaces boost the dissociation of water and production of H intermediates, and H is then easily adsorbed on Pt surfaces.

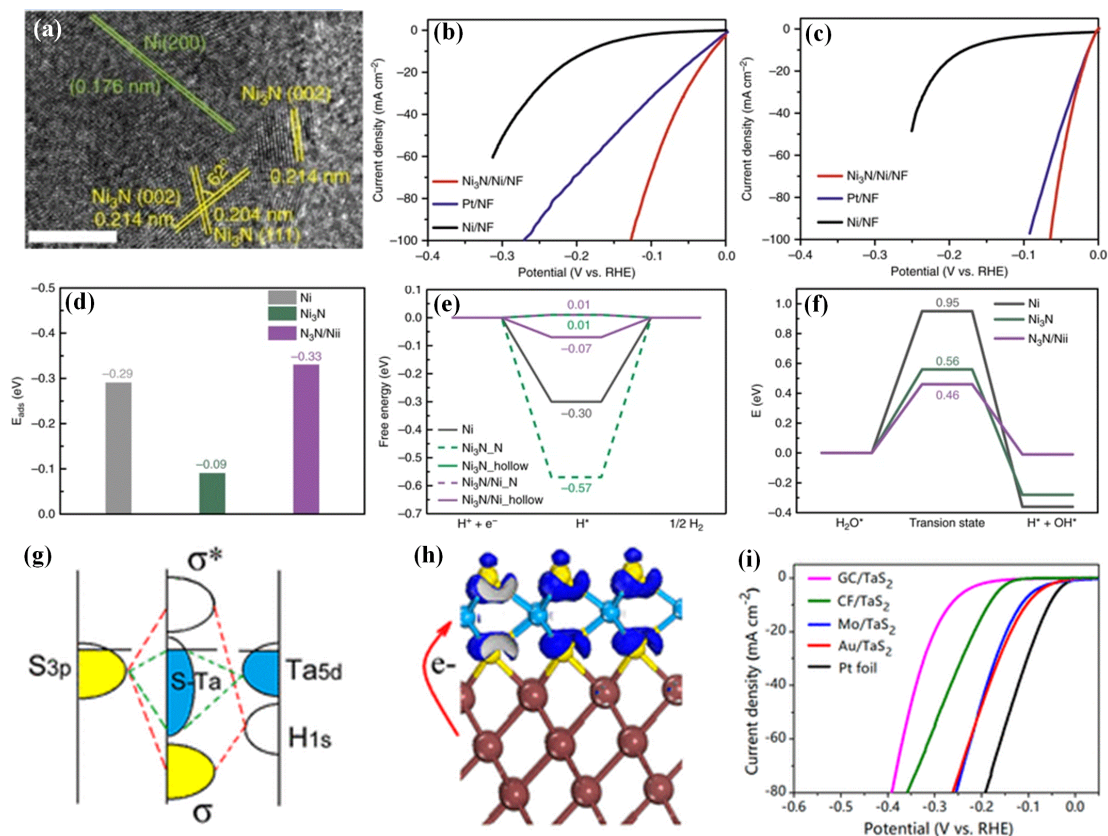


Figure 6. (a) The HRTEM image of Ni₃N/Ni catalyst, scale bar: 5 nm. The corresponding LSV curves for HER in 1.0 M potassium phosphate (KPi) buffer (b) and 1.0 M KOH electrolyte (c). (d) Adsorption energy of H₂O molecule over different sites. (e) The ΔG_{H^*} and (f) reaction barrier of H₂O dissociation over Ni, Ni₃N, and Ni₃N/Ni. Reproduced with permission.⁷⁶ Copyright 2018, Nature Publishing Group. (g) Schematic diagram of molecular orbitals for H-TaS₂. (h) Charge density distribution of Au/TaS₂, where Au, Ta, S, and H are shown as brown, blue, yellow, and white spheres, respectively. (i) The electrocatalytic HER performance of TaS₂ samples on different substrates. Reproduced with permission.⁷⁷ Copyright 2019, American Chemical Society.

Sun et al. reported that interfacing Ni₃N and Ni is a promising method of increasing active sites and engineering electronic structures for highly active HER in aqueous media, in which Ni₃N/Ni was synthesized through cathodic electrodeposition, followed by facile thermal nitridation.⁷⁶ Figure 6a shows the HRTEM image of as-prepared Ni₃N/Ni sample with interfaces of hexagonal Ni₃N and Ni metal. Lattice fringes clearly indicated the exposed faces of the Ni₃N/Ni sample are (111) and (002) planes of Ni₃N,

and the (200) plane of cubic Ni. Figure 6b and 6c displayed electrocatalytic HER performances of Ni₃N/Ni on Ni foams in H₂-saturated electrolytes, where the Ni₃N/Ni/NF electrode showed remarkable η_{10} of 19 and 12 mV in 1.0 M KPi buffer and 1.0 M KOH, respectively. However, the Ni/NF electrode and Pt/NF displayed mediocre HER performances, suggesting the critical role of the interfaces between Ni₃N and Ni. DFT was conducted to further investigate the role of interfaces in improving catalytic activities. The ΔG_{H^*} values at two positions of Ni₃N/Ni_{_N} and Ni₃N/Ni_{_hollow} (Figure 6d) are 0.01 and - 0.07 eV, which are smaller than those of pure Ni (- 0.3 eV) and pure Ni₃N site (- 0.57 eV). This finding confirms that the interface effects could reduce H binding affinity on the Ni₃N/Ni surface. Figure 6e displays the adsorption and dissociation of H₂O over electrocatalyst surfaces, that are paramount steps of HER in neutral and alkaline conditions. The adsorption energies along with the optimized structures suggest that the H₂O molecules tend to reside along the interfaces, which could greatly facilitate the subsequent H₂O dissociation on Ni₃N/Ni. The diagrams of the H₂O dissociation barrier (Figure 6f) show that Ni₃N/Ni holds the lowest energy barrier of 0.50 eV, smaller than those of Ni₃N and Ni. These DFT results proved that interface effects could engineer the electronic structures to further optimize the H and H₂O binding affinities, reduce the reaction barriers, and facilitate water dissociation. Liu and co-worker proposed that the HER performances of metallic 2D TaS₂ can be tuned via lattice mismatch and electron injection between electrocatalysts and the underlying substrates caused by interfacial engineering.⁷⁷ A series of 2D TaS₂ was successfully grown on different substrates via two-zone chemical vapor deposition. The schematic of molecular orbitals for H-TaS₂ (Figure 6g) shows that Ta and H atoms donate electrons to S. The charge density distribution (Figure 6h) displays that electrons are injected TaS₂ from the metallic substrates, which could weaken S–H and S–Ta bonds and lead to smaller ΔG_{H^*} . Consequently, TaS₂ on Au foil offered the best enhanced performances with lowest overpotential and smallest charge transfer resistance in the catalytic LSV curves (Figure 6i), revealing the validity of interface effects for engineering catalysts. He and co-workers fabricated a Ravenala leaf-like

$W_xC@WS_2$ heterostructure on carbon fibers (CFs) through carbonizing WS_2 nanotubes (NTs).⁷⁸ During synthesis, the outer walls of the WS_2 NTs were partially unzipped and had the appearance of nanoscale W_xC , which was attached to the inner tubes. LSV curves with iR-correction in Figure 7a displays that this $W_xC@WS_2$ catalysts required a low η_{10} of 146 mV, which is 172.7 and 46 mV smaller than those of pure WS_2 and W_xC at the same conditions, respectively, suggesting the crucial roles of interface effects. Figure 7b shows that the related Tafel slope of $W_xC@WS_2-20$ was 61 mV dec^{-1} , indicating a two-electron-transfer process with Volmer–Heyrovsky mechanism. This value is also smaller than those of pure WS_2 (110 mV dec^{-1}) and W_xC (68 mV dec^{-1}). DFT calculations revealed that interface effects could induce charge redistribution in heterostructures and optimize the adsorption and desorption abilities of catalysts to boost their HER performances. Free energy diagram showed that the ΔG_{H^*} over pure W_2S is approximately 2.26 eV, suggesting that the W_2C tightly binds H atoms and further hinders the H_2 desorption on its surface. When interfacing W_2C with WS_2 , an electron transfer of 0.12 e from W_2C to WS_2 was detected in the charge redistribution in $W_2C@WS_2$ heterostructure (Figure 7c and 7d), which strongly implied the decrease of its ability of binding H atoms. In 2019, the engineered W_2N/WC heterostructures with abundant interfaces were prepared via a facile solid-state synthesis method.⁷⁹ During this process, volatile CN_x species generated from dicyanodiamide at high temperature could be trapped by WO_3 nanorods, and then the heterostructure catalysts were produced. Interestingly, the components in samples can be regulated by altering the synthesis temperature. When pyrolysis temperatures of 600 °C, 700 °C and 800 °C were applied, the WO_3/W_2N heterostructures, pure W_2N and W_2N/WC heterostructures were obtained, respectively. The corresponding models and HRTEM images of WO_3/W_2N , pure W_2N and W_2N/WC heterostructures were shown in Figure 7e-7j. From HRTEM image of W_2N/WC sample, the lattices with 0.238 nm for W_2N (111) plane and 0.252 nm for WC (100) plane were clearly observed, confirming the abundant interfaces between W_2N and WC. The XPS spectra showed that the binding energy of W 4f in W_2N/WC was higher (1.0 eV) than that in pure W_2N , stating the extra charges

in the W 4f side and charge accumulation in W₂N due to these existing interfaces. As OER electrocatalysts, the W₂N/WC heterostructures displayed excellent performances with a low η_{10} of 320 mV, superior to that of the W₂N and WC catalysts (Figure 7k). The Tafel slopes plots showed that the W₂N/WC heterostructures possessed smaller value of approximately 94.5 mV dec⁻¹ than other samples, and the TOF value of W₂N/WC heterostructures was 0.15 s⁻¹ at 1.60 V, which is also higher than WO₃/W₂N (0.1 s⁻¹), and W₂N (0.03 s⁻¹). For HER, the W₂N/WC electrocatalyst exhibited a small η_{10} of 148.5 mV and a low Tafel slope value of 47.4 mV dec⁻¹ (Figure 7l). DFT and XANFS analysis revealed that interfaces in W₂N/WC synergistically facilitated charge transfer, tremendously enhancing the electrocatalytic performances. Inspired by these results, many hybrid electrocatalysts with abundant interfaces have been reported, where more active sites were created, and the electronic structures were regulated for greatly boosting the electrocatalytic performances.⁸⁰⁻⁸⁸ However, the fundamental mechanisms and structure-activity relationships of interface effects between active components still remain elusive because of their complexity.

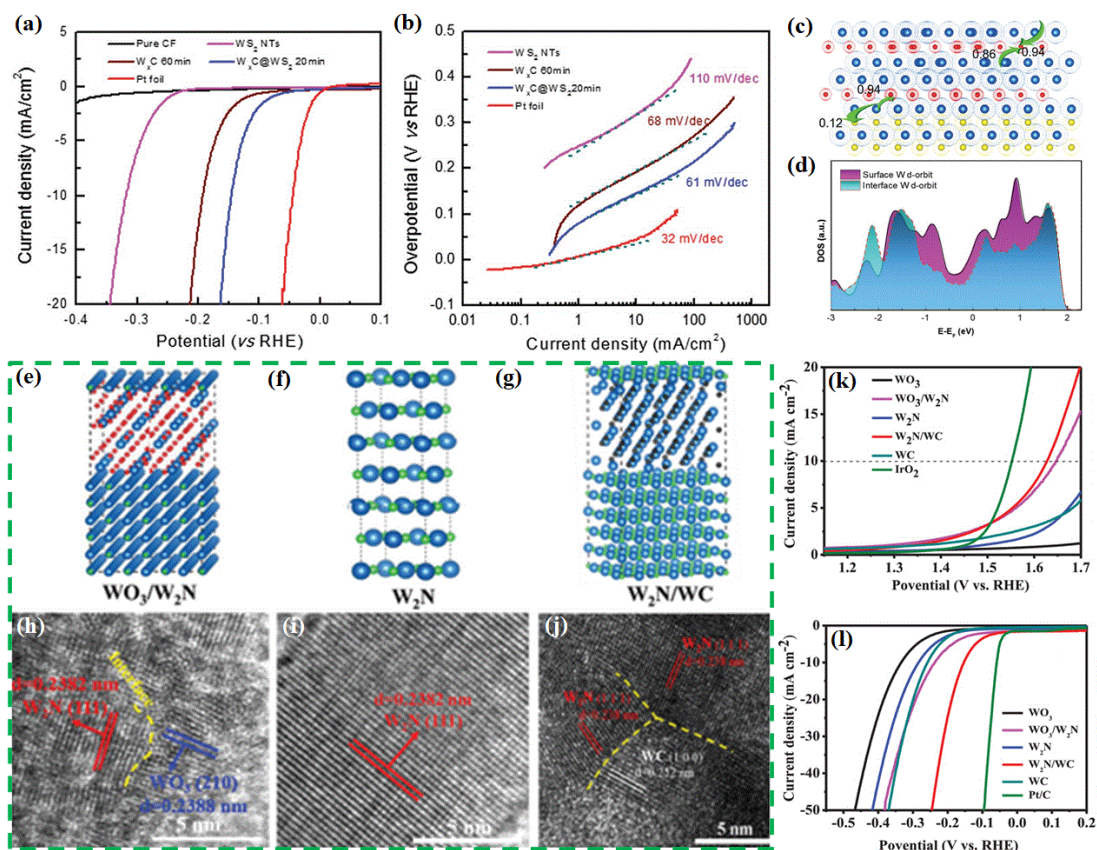


Figure 7. (a) The HER LSV curves and (b) Tafel slope plots for obtained $W_xC@WS_2$ -20 and reference samples. (c) Calculated charge redistribution in $W_2C@WS_2$ heterostructure and (d) DOS comparison of the W located at different position. Reproduced with permission.⁷⁸ Copyright 2017, Wiley-VCH. (e-g) The representative models and (h-j) their corresponding HRTEM images of obtained WO_3/W_2N , W_2N , and W_2N/WC , respectively. (k) Experimental OER LSV curves, and (l) HER LSV curves of WO_3/W_2N , W_2N , W_2N/WC , and WC heterostructure electrocatalysts and noble metal catalysts. Reproduced with permission.⁷⁹ Copyright 2017, Wiley-VCH.

3.3. Engineering by crystal face

Principally, the catalytic activities of electrocatalysts for a specific reaction are highly dependent on the arrangement of atoms on the exposed surfaces, determining their adsorption and desorption abilities, and the amount of active centers. Therefore, regulating the type of the exposed crystallographic plane could greatly improve the performances of electrocatalysts for various reactions. Efforts have been devoted to studying the relationships between faceting and catalytic performances during the past several decades.⁸⁹⁻⁹¹ The high-index faceted nanocrystals generally possess higher energy surfaces, which could increase specific activity, while the low-index faceted materials with lower energy surfaces could provide good catalytic stability.⁹²⁻⁹⁴ For HER electrocatalysis, the previous works approximately the dependence of HER activities vs. Pt catalyst facets have uncovered that the activities decreased with the decreasing activation energies of $(110) > (100) > (111)$.^{95,96} Furthermore, Markovic and co-workers in 2014 reported a study on the functional law between the activity and stability for OER of Ru single-crystal catalysts.⁹⁷ Consequently, the OER stabilities of Ru crystals increase in the order $(001) > (110) > (111)$. The (001) face with Ru atoms possessing the highest coordination numbers and the lowest surface energies, is the most stable morphologically, which could reduce the generation and dissolution of higher state Ru species. These findings inspire us to regulate the exposed crystal plane surfaces where the electrochemical reactions occur to boost the electrocatalytic

performances of TM-based nanocatalysts.⁹⁸⁻¹⁰¹ For instance, Ma and his co-workers synthesized surface-tailored Co_3O_4 supported on N-doped reduced graphene oxide (N-rGO) to regulate the active sites of Co_3O_4 spinel for OER.¹⁰² As shown in Figure 8a, three Co_3O_4 nanocrystals with different shapes and terminal faces anchored on N-rGO were prepared through a hydrothermal method. The morphologies of objective Co_3O_4 nanostructures on 2D N-rGO were easily tuned from nanocube (Nc) to nanooctahedron (NTO) and then nanopolyhedron (NP) using this synthesis process by simply changing the dosage of $\text{Co}(\text{NO}_3)_2$, $\text{NH}_3\cdot\text{H}_2\text{O}$ and corresponding GO solution. These as-prepared $\text{Co}_3\text{O}_4\text{-NC/N-rGO}$, $\text{Co}_3\text{O}_4\text{-NTO/N-rGO}$ and $\text{Co}_3\text{O}_4\text{-NP/N-rGO}$ were terminated with $\{001\}$, $\{001\} + \{111\}$, and $\{112\}$ planes, respectively, which were featured by different concentrations and distributions of $\text{Co}^{2+}/\text{Co}^{3+}$ active sites on these exposed surfaces. The surface atomic arrangements in the $\{001\}$, $\{111\}$ and $\{112\}$ planes in the Co_3O_4 are displayed in Figure 8b–d, where the $\{001\}$ or $\{111\}$ planes only possess tetrahedrally coordinated Co^{2+} ($\text{Co}^{2+}_{\text{Td}}$) sites under normal condition, while the $\{112\}$ plane not only has $\text{Co}^{2+}_{\text{Td}}$, but also possesses octahedrally coordinated Co^{3+} ($\text{Co}^{3+}_{\text{Oh}}$) sites. In theory, the $\text{Co}^{3+}_{\text{Oh}}$ sites could act as superior active sites to $\text{Co}^{2+}_{\text{Td}}$ species in efficient adsorption, activation and desorption processes, suggesting that the $\{112\}$ faceted $\text{Co}_3\text{O}_4\text{-NP/N-rGO}$ with abundant $\text{Co}^{2+}_{\text{Td}}$ and $\text{Co}^{3+}_{\text{Oh}}$ sites is more active than $\text{Co}_3\text{O}_4\text{-NTO/N-rGO}$ and $\text{Co}_3\text{O}_4\text{-NC/N-rGO}$ for OER. Electrochemical results in Figure 8e exhibits that $\text{Co}_3\text{O}_4\text{-NP/N-rGO}$ terminated by the unusual $\{112\}$ crystal plane owns superior OER performances than that of $\text{Co}_3\text{O}_4\text{-NC/N-rGO}$ and $\text{Co}_3\text{O}_4\text{-NTO/N-rGO}$. Ho and co-workers successfully prepared high-index $\{112\}$ faceted and defective Co_3O_4 nanosheets via a facile hydrothermal and NaBH_4 reduction strategy.¹⁰³ Remarkably, the obtained porous Co_3O_4 nanosheets with exposed $\{112\}$ faces exhibited better activities toward OER with a lower η_{10} of 318 mV than those of $\{110\}$ or $\{111\}$ faceted porous Co_3O_4 nanosheets. The exposed $\{112\}$ high-index facets with higher ratio of $\text{Co}^{2+}/\text{Co}^{3+}$ contributed to accelerating charge transfer and increasing active sites. In addition, $\text{Ni}_3\text{S}_2/\text{NF}$ electrode consisted of high-index faceted Ni_3S_2 nanosheets on nickel foam was synthesized by Zou et. al. by a in situ synthetic method.¹⁰⁴ As binder-

free electrodes, the obtained Ni₃S₂/NF materials showed highly active bifunctional performances towards both HER and OER. As depicted in Figure 8f and 8g, the high-index faceted Ni₃S₂/NF electrode needs small η_{10} of 223 and 260 mV for HER and OER in basic electrolyte, respectively. Moreover, the self-supported Ni₃S₂/NF electrode showed approximate 100% FE and remarkable durability (> 200 h) for both HER and OER. The activities for HER of the different faced surfaces were explored using DFT computations (Figure 8h-j). Three different kinds of S-sites on Ni₃S₂ (210) surface were simulated and the calculated ΔG_{H^*} values were 0.623 eV, 0.520 eV and 1.018 eV, which are smaller than that on the (001) surface, confirming the HER activity is higher on (210) surface. The S-sites with lower coordination number located at the deges of (210) surface mainly contribute to the excellent oerformances. Mu's group revealed that the exposed (222) plane in tantalum carbide (TaC) electrocatalysts could be more effective than other facets toward catalyzing HER by using theoretical calculations, and subsequently a new "micro-cutting-fragmentation" method was presented to synthesize the TaC with abundant high-index (222) exposed facets.¹⁰⁵ Calculated band structure in Figure 8k shows that no band gap is detected for all facets of TaC, implying its high conductivity, which is quite important for electrocatalytic HER. As shown in Figure 8l, the high-index TaC (222) facet displays a smaller ΔG_{H^*} value (- 0.23 eV) than (311), (220), (200) and (111) facets, further suggesting its best electrocatalytic activity over (222) facet. The as-prepared TaC NCs@C catalysts display a low onset potential (Figure 8m), a small Tafel slope (Figure 8n), and excellent stability for HER.

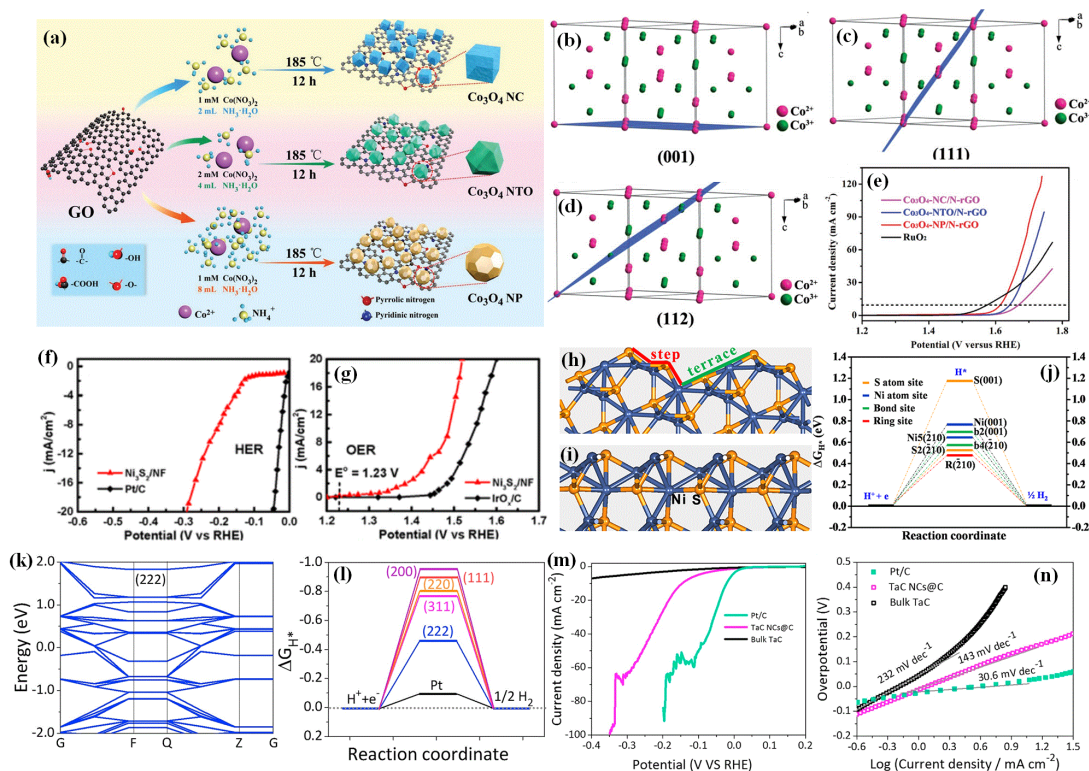


Figure 8. (a) Schematic illustration of synthesizing Co_3O_4 nanocrystals with different . (b-d) The $\text{Co}^{2+}/\text{Co}^{3+}$ surface atomic configurations on (001), (111) and (112) planes in Co_3O_4 . (e) LSV curves towards OER in 1 M KOH aqueous solution. Reproduced with permission.¹⁰² Copyright 2017, Wiley-VCH. Steady-state current densities vs. applied potentials over high-index faceted Ni_3S_2 nanosheet arrays for HER (f) and OER (g). The most optimal terminations of (210) (h) and (001) (i) surfaces of Ni_3S_2 . (j) The ΔG_{H^*} diagram of HER calculated over (210) and (001) surfaces of Ni_3S_2 . Reproduced with permission.¹⁰⁴ Copyright 2015, American Chemical Society. (k) Band structure of high-index TaC (222) facets obtained by DFT. (l) Calculated ΔG_{H^*} diagram of HER for high-index (222) facet, relatively low-index (111), (200), (220) and (311) facets of TaC as well as Pt reference. (m) and (n) The LSV curves and corresponding Tafel plots in 0.5 M H_2SO_4 solution. Reproduced with permission.¹⁰⁵ Copyright 2017, Elsevier Inc.

In conclusion, tuning the density of highly exposed catalytically favorable faces in various nanomaterials is a promising strategy to reconstruct active sites in the catalysts, and optimize their related adsorption and desorption energies to boost the electrocatalytic performances. Numerous efforts have been made to develop facile

strategy for tuning the exposed faces,¹⁰⁶⁻¹¹² however, due to the different surface energies of exposed faces, stable and catalytically favorable pure faces always evolve or disappear during their synthesis or application process. Therefore, engineering the nanocatalysts with favorable exposed faces to significantly improve their catalytic performances toward is still a challenge yet.

3.4. Engineering by elemental doping

Introducing other metal or nonmetal elements with different electron configurations into the lattice of TM-based electrocatalysts can lead to subtle distortion of the atomic arrangement, further regulate the active centers, and increase the active sites, change the electronic structures, and markedly tune the adsorption abilities of the catalyst surfaces. Therefore, engineering the catalysts by elemental doping has been a potential method to boost their water splitting performances.¹¹³⁻¹¹⁶ For instance, Wu's group in 2010 synthesized Ni-doped Co_3O_4 nanowire arrays anchored onto a Ti foil. Results revealed that Ni dopants could lead to enhanced electronic conductivities and more active sites of the Co_3O_4 , further improving OER performances.¹¹⁷ Zhang and co-workers proposed an N-doped CoP electrocatalyst, and the LSV curves (Figure 9a) displays that the N-doped CoP sample on CC requires a small η_{10} of 42 mV; this is better than pure CoP, indicating that N doping could greatly boost the HER activities of CoP.¹¹⁸ The effect of N doping on HER performances was explored by DFT calculations. As depicted in Figure 9b, the CoP (101) surfaces possessed a ΔG_{H^*} value of -0.52 eV, suggesting a strong adsorption of H. While after N doping, the related ΔG_{H^*} value increased to -0.14 eV, which is more thermo-neutral than that of pure CoP. Moreover, the calculated DOS of CoP and N doped CoP in Figure 9c illustrated that N doping could lead to downshift of d-band and weaken the H adsorption on their surface because N has stronger electronegativity than phosphorus. Yan and his co-workers revealed that elemental doping could efficiently modulate the electrocatalytically active center of Cu_7S_4 for OER.¹¹⁹ As shown in the LSV curves (Figure 9d), the Co- Cu_7S_4 with the

atomic ratio of Co/(Co+Cu) of 0.07 (denoted as Co-Cu₇S₄-0.07) exhibited the best OER activity with a small η_{10} of 270 mV, superior to bare Cu₇S₄ and commercial IrO₂. Figure 9e displays the profiles of the free energy changes of OER over Cu₇S₄ and Co doped Cu₇S₄, and Figure 9f shows the feasible OER mechanism for the Co engineered Cu₇S₄ catalyst. These results stated the Co doped Cu₇S₄ with modified electronic structure could accelerate electron transfer between the active sites, increase the active sites, and lower the energy barriers. Similarly, Zhao and his co-workers reported that cobalt covalent doping could bring enhanced HER and OER bifunctionalities to MoS₂.¹²⁰ The HER LSV curves in Figure 9g exhibit that Co-MoS₂ with Mo/Co molar ratio of 21 (denoted as Co-MoS₂/BCCF-21) displayed superior HER performances with a low onset potential of - 0.02 V, which is better than that of MoS₂/BCCF. The OER LSV curves in Figure 9h of BCCF, MoS₂/BCCF, Co-MoS₂/BCCF-21, and commercial RuO₂ indicated that Co-MoS₂/BCCF-21 catalyst can catalyze oxygen evolution at an onset potential of 1.45 V, which is only 0.06 V larger than RuO₂ (1.39 V), and better than MoS₂/BCCF. These results certified that covalent cobalt doping into MoS₂ could contribute to dramatically enhanced HER and OER activities. Figure 9i shows the optimized configuration of Co covalently doped MoS₂ and the calculated DOS, which exhibits the overlapped 3d states of Co with 3p states of its neighboring S atoms in MoS₂. The calculation illustrated that initial MoS₂ semiconductor possessed a bandgap of 1.70 eV, while the MoS₂ after Co doping possesses metallic characteristics with a bandgap (0 eV), which is quite beneficial for water splitting.

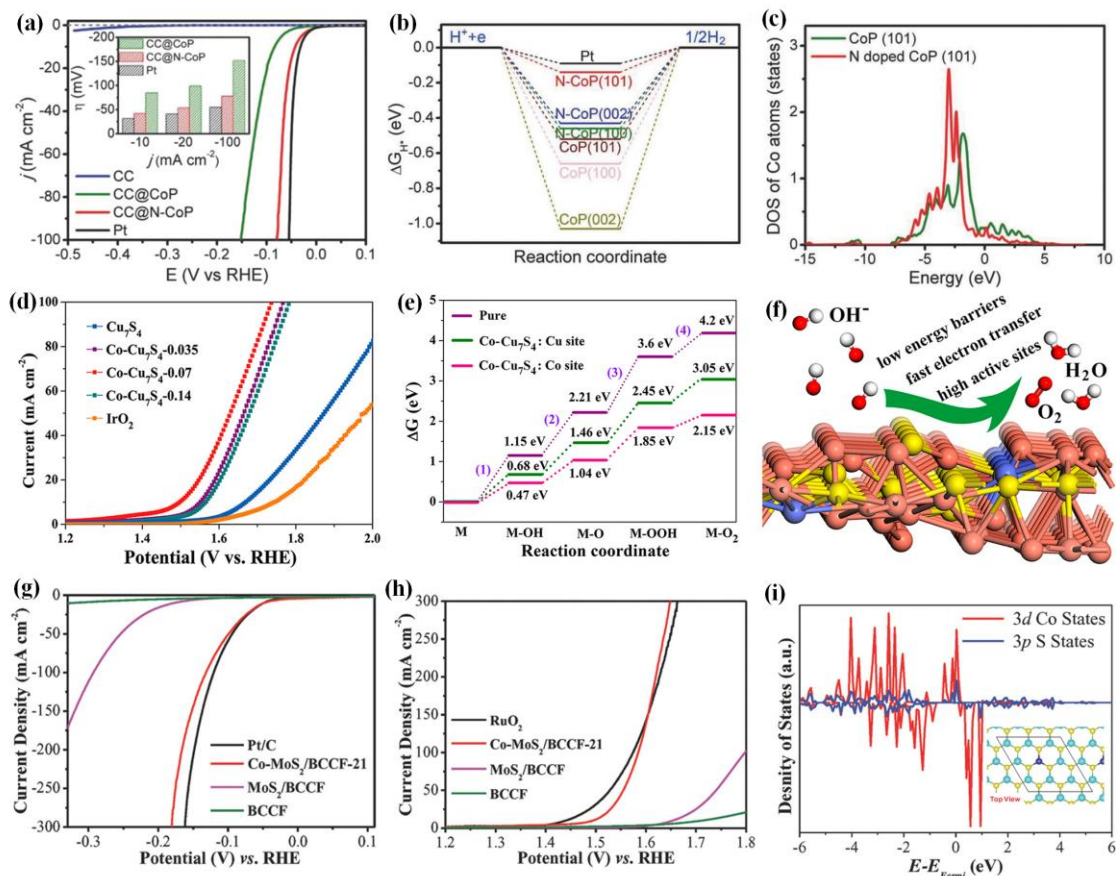


Figure 9. (a) The LSV curves for HER of CC, CC@CoP, CC@N-CoP, and Pt catalysts, (inset: corresponding η). (b) ΔG_{H^*} diagram at the Co–Co bridge site on the surfaces of CoP and N-CoP. (c) Calculated DOS of Co atoms on the CoP (101) surface with or without N doping. Reproduced with permission.¹¹⁸ Copyright 2018, Wiley-VCH. (d) The LSV curves for OER of Cu_7S_4 and Co- Cu_7S_4 with different Co doping amounts. (e) Gibbs free energy diagram over pure Cu_7S_4 , Cu site of Co- Cu_7S_4 and Co site of Co- Cu_7S_4 . (f) The feasible OER mechanism for the Co engineered Cu_7S_4 catalyst. Reproduced with permission.¹¹⁹ Copyright 2017, American Chemical Society. (g) The LSV curves for HER of BCCF, MoS_2/BCCF , Co- $\text{MoS}_2/\text{BCCF-21}$, and Pt/C electrodes and (h) LSV curves for OER of BCCF, MoS_2/BCCF , Co- $\text{MoS}_2/\text{BCCF-21}$, and RuO_2 electrodes. (i) Calculated DOS of 3d Co and 3p S states (insert: top views of the Co doped MoS_2 structure with a Mo/Co ratio of 8:1). Reproduced with permission.¹²⁰ Copyright 2018, Wiley-VCH.

Recently, single-atom doping has emerged as a promising strategy to tailor the

electronic structures, increase the electroactive site densities, facilitate electron transfer, and enhance corresponding stabilities of TM-based electrocatalysts for water splitting.¹²¹⁻¹²³ For example, Pt single atoms were introduced into VS₂ nanosheets via a cost-effective optothermal approach by Zhang et al., which can greatly boost the HER activities of VS₂.¹²⁴ In this work, the structures of Pt including single atoms (SAs), clusters and NPs on VS₂ nanosheets were well-controlled by optimizing the concentration of chloroplatinic acid. HAADF-STEM image (Figure 10a) and XAFS characterizations of as-prepared 0.1Pt/Vs₂/CP electrode revealed that numerous atomically dispersed Pt were anchored on the VS₂ surface, and no Pt clusters or particles appeared. After Pt single atom doping, the HER performances of 0.1Pt/Vs₂/CP were remarkably enhanced compared with those of pure VS₂/CP electrode. Figure 10b shows that the η_{10} of 0.1Pt/Vs₂/CP electrode is 135 mV smaller than that of VS₂/CP. The mass activity of Pt/Vs₂/CP with Pt SAs decorating was 12 times higher than Pt/C catalyst. DFT simulations revealed that Pt single atom doping on the VS₂/CP makes the ΔG_{H^*} value closer to zero (Figure 10c) and enhances the charge-transfer kinetics, significantly enhancing HER activity. Similarly, Xing and co-workers reported that Pd atom doping could chemically activate the molybdenum disulfide (MoS₂) surface basal plane for efficiently catalyzing HER.¹²⁵ Using a spontaneous interfacial redox method, Pd single atoms were doped at the Mo sites, which simultaneously introduced sulfur vacancy into MoS₂ due to the Mo redox process and transformed the 2H-MoS₂ into the stabilized 1T-MoS₂, which was proved by Figure 10d. K-edge EXAFS spectra and fitting curves (Figure 10e) shows that the Mo–S and Mo–Mo peak intensities of MoS₂ decreased after Pd doping, confirming the generation of sulfur vacancy and the rearrangement of Mo atoms. From Figure 10f, we can find that the MoS₂ doped with single Pd atoms displayed a lower η_{10} of 78 mV, compared with MoS₂ without Pd doping. DFT calculations revealed that the sulfur sites next to the Pd atoms exhibited low hydrogen adsorption energy. Calculated pDOS showed that S received electrons from the adjacent Mo atoms, leading to a weaker binding with hydrogen and higher HER activity. In addition, Ni(OH)₂ nanosheet electrocatalysts doped with atomically dispersed W for

OER catalysis were fabricated by Ma and his co-workers.¹²⁶ The atomically doping of W element and corresponding oxidized electronic structure (W^{6+}) of W were proved by XAS measurements and corresponding normalized XANES spectra. The HAADF-STEM image of the obtained sample in Figure 10g directly confirmed the single atom W in $Ni(OH)_2$ lattice according to these light spots from W element. Oxidation peaks of Ni^{2+} into $Ni^{3/4+}$ in LSV curves displayed a slight positive shift for the W- $Ni(OH)_2$ nanosheets, suggesting the single atom W doping could boost carrier migration. As shown in Figure 10h and 10i, the W- $Ni(OH)_2$ catalysts exhibited a lower η_{10} (237 mV) and a smaller Tafel slope value (33 mV dec^{-1}) than $Ni(OH)_2$. Theoretical results (Figure 10j) revealed that W^{6+} sites in $Ni(OH)_2$ matrix contributed to H_2O adsorption and O radical generation, suggesting that a single atom W could contribute to H_2O adsorption, generate adsorbed OH^- group and O radical, and further dramatically enhance the OER performances. Luo and his co-workers reported that Cr-doping could synergistically regulate H_2O and binding abilities over Co_4N , further resulted in exceptional HER performances in alkaline media.¹²⁷ Therefore, elemental doping has been widely used as is a promising method to increase the active site densities, tuning the electronic structures, optimize the adsorption of reactant species and reduce the related reaction barriers of various TM-based materials for efficient electrocatalysis.¹²⁸⁻¹³⁹

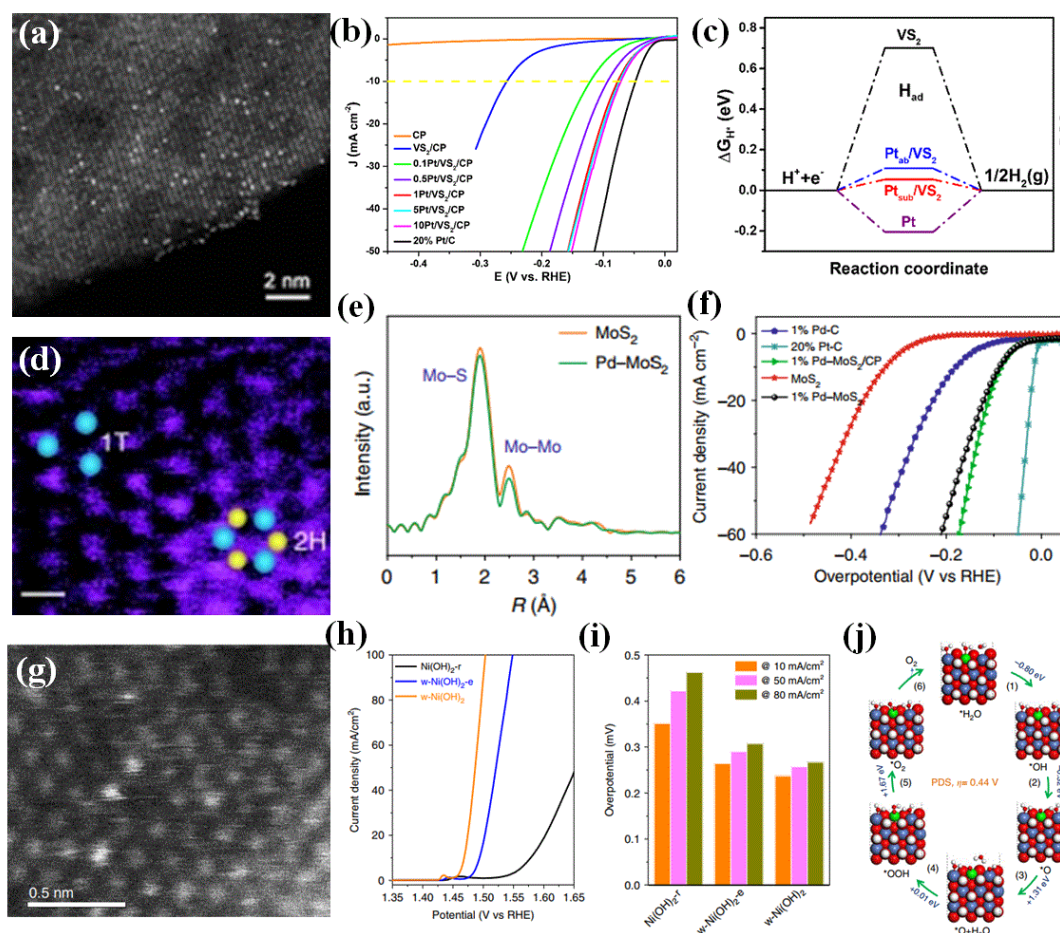


Figure 10. (a) HAADF-STEM image of single-atom Pt-decorated VS₂ nanosheets. (b) The LSV curves for HER of pure CP, pure VS₂/CP, different-amount Pt-decorated VS₂/CP and Pt/C. (c) ΔG_{H^*} diagram over pure VS₂, Pt_{sub}/VS₂, Pt_{tab}/VS₂, and Pt particles. Reproduced with permission.¹²⁴ Copyright 2020, American Chemical Society. (d) HAADF-STEM image of the 1%Pd–MoS₂ sample. Scale bar: 1 nm. Blue ball: Mo and yellow ball: S. (e) Fourier transform curves for Mo K-edge of the EXAFS spectra of MoS₂ and Pd-MoS₂. (f) The LSV curves for HER with iR correction in 0.5 M H₂SO₄ media. Reproduced with permission.¹²⁵ Copyright 2018, Nature Publishing Group. (g) HAADF-STEM image of single W-Ni(OH)₂ sample. (h) The LSV curves for OER with 95%-correction. (i) The η at current densities of 10, 50, 80 mA cm⁻² over different electrodes. (j) Mechanism study of OER over W-doped Ni(OH)₂ by DFT calculations. Red, white, green, and blue ball: oxygen, hydrogen, nickel, and tungsten atom, respectively. Reproduced with permission.¹²⁶ Copyright 2019, Nature Publishing

Group.

3.5. Engineering by defects

The defects, including point defects, line defects, two-dimensional defects, and three-dimensional defects, could cause distortions of the structure in the crystalline solids, which further drastically change their electron distribution and band structure. Therefore, defect-engineering methods can play vital roles in regulating electrochemical water splitting activities and stabilities of TM-based electrocatalysts through regulating their conductivities, active site centers, and adsorption/desorption abilities. In this section, the roles of oxygen vacancy defects, cation vacancy defects, and multi-vacancy defects in improving the electrochemical reaction performances are carefully pointed out.

3.5.1. Engineering by oxygen vacancy defects

Oxygen vacancy, as one of the most common anion vacancies in the TM oxides has usually been created to regulate the electrocatalytic performances. Upon oxygen vacancies are introduced into TM oxide-based catalysts, the electronic structures could be greatly changed, and then the metal oxides can be transformed from a conventional semiconductor with low conductivity into a degenerate one with higher conductivity. These tuned electronic structures by oxygen vacancies could also reduce the reaction barriers of HER or OER and optimize the adsorption abilities of regent species over the catalysts, finally leading to enhanced catalytic performances. Therefore, introducing oxygen vacancies into TM-based oxides has been applied widely to directly and effectively tune the intrinsic electrocatalytic performances.¹⁴⁰⁻¹⁴⁶ For instance, Zeng and his co-workers prepared WO₃ nanosheets with oxygen vacancies as HER catalysts.¹⁴⁷ DFT simulation predicted introducing oxygen vacancies into WO₃ can tune their electronic structures, improve their conductivities and optimize the hydrogen adsorption abilities. As depicted in Figure 11a, the DOS of bulk WO₃ without oxygen vacancy shows a typical semiconductor character, where Fermi level locates within band gap. Nevertheless, when oxygen vacancies are introduced, new energy levels

appear at conduction band minimum and its band gap is narrowed. Moreover, the Fermi level is located at the conduction band minimum of W 5d, suggesting the formation of a degenerate semiconductor. Moreover, the calculated ΔG_{H^*} diagram in Figure 11b displays that the ΔG_{H^*} value of perfect WO_3 is 2.3 eV, and when oxygen vacancies are introduced, the ΔG_{H^*} value is reduced and comparable to that of platinum. Experimentally, the as-prepared WO_3 nanosheets with oxygen vacancies exhibited excellent activities with a low η_{10} of 38 mV (Figure 11c) and a small Tafel slope of 38 $mV\ dec^{-1}$, implying that introducing oxygen vacancies could efficiently boost the HER performances. Shi and his co-workers reported a facile method to synthesize an effective HER electrocatalyst of Pt/def- WO_3 @CFC with platinum atom clusters dispersed on oxygen vacancy-rich WO_3 . For HER catalysis, this as-fabricated electrocatalyst exhibited Pt/C like performances, which were partly generated from oxygen vacancies in WO_3 nanoplates.¹⁴⁸ Moreover Zheng and his co-workers proposed a facile method to prepare Co_3O_4 nanowires with rich oxygen vacancies via the $NaBH_4$ aqueous solution-treatment at room temperature (Figure 11d).¹⁴⁹ XRD and XPS results confirmed the generation of oxygen vacancies in Co_3O_4 nanowires (NWs) after $NaBH_4$ treatment. The formation energy plots (Figure 11e) from DFT calculation shows that the Vo^{2+} possesses the lowest formation energy, suggesting oxygen vacancies are most likely formed as Vo^{2+} . The calculated total DOS and projected DOS (Figure 11f) indicate that Co_3O_4 NWs with oxygen vacancies are equipped with a new state within their band gap. In these states, the electrons associated with the Co-O bonds become more delocalized, leading to higher electrical conductivity and better electrocatalytic performance than pristine Co_3O_4 . The Co_3O_4 with oxygen vacancies exhibited enhanced OER performances compared with pure Co_3O_4 , with a small onset potential of 1.52 V (Figure 11g), and a low Tafel slope of 72 $mV\ dec^{-1}$ (Figure 11h). These experimental results confirmed that the oxygen vacancies in metal oxides could result in new gap states, dramatically improving the conductivity and boosting their electrocatalytic performances.

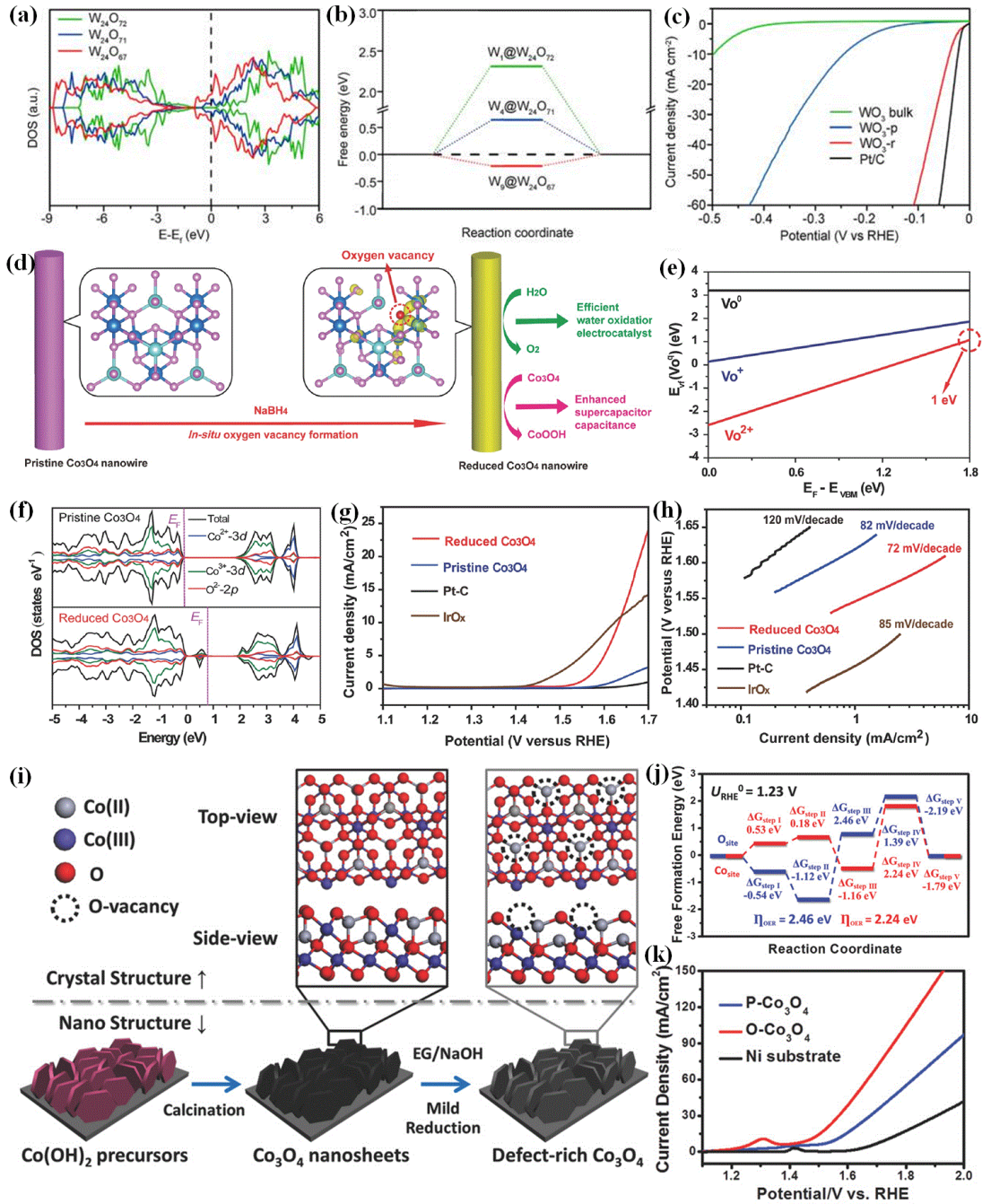


Figure 11. (a) The calculated partial DOS of W in WO_3 with different oxygen vacancies. (b) Free-energy diagram on WO_3 (010) face with oxygen vacancies. (c) LSV curves for HER of the WO_3 bulk, WO_{3-p} NSs, WO_{3-r} NSs and Pt/C. Reproduced with permission.¹⁴⁷ Copyright 2017, American Chemical Society. (d) Schematic illustration of introducing oxygen vacancy into Co_3O_4 NWs. (e) Calculated formation energies of Co_3O_4 with vacancies. (f) TDOS and PDOSs of the perfect Co_3O_4 and defective Co_3O_4 . (g) LSV curves for OER of the Co_3O_4 NWs with/without defects, IrO_x and Pt/C in 1 M

KOH. (h) Tafel plots derived from LSV curves. Reproduced with permission.¹⁴⁹ Copyright 2014, Wiley-VCH. (i) Schematic illustration of introducing oxygen vacancies into single-crystalline Co_3O_4 nanosheets. (j) Free energy diagram over the Co_3O_4 configuration with/without oxygen vacancies. (k) LSV curves for OER of obtained Co_3O_4 with oxygen vacancy, pristine Co_3O_4 catalysts, and Ni substrate in 1 M KOH media. Reproduced with permission.¹⁵⁰ Copyright 2018, Wiley-VCH.

Afterwards, Sun et al. presented a solvothermal reduction approach (Figure 11i) with ethylene glycol as the reducing agent to create oxygen vacancies in the single-crystalline Co_3O_4 nanosheets.¹⁵⁰ Corresponding DFT calculation (Figure 11j) showed the lower OER activation energy value of 2.24 eV on Co_3O_4 nanosheet surface with oxygen vacancies (2.46 eV on pristine Co_3O_4), implying advantageous OER kinetic over defective Co_3O_4 . The band gap for pristine Co_3O_4 is 1.93 eV, while a narrow band gap of 1.74 eV was obtained after the creation of oxygen vacancies into Co_3O_4 , confirming high conductivity of Co_3O_4 with oxygen vacancies. XPS and XANES experimental results confirmed that the oxygen vacancies were generated on the surface of Co_3O_4 , and the lower Co coordination number of defected Co_3O_4 than that of pristine Co_3O_4 nanosheets endowed their high activities. The LSV curves in Figure 11k displays that the onset overpotential is lowered from 300 mV to 220 mV after introducing oxygen vacancies in to Co_3O_4 . In addition, the defective Co_3O_4 with rich oxygen vacancies also exhibited smaller Tafel slope value (49.1 mV dec^{-1}) than perfect Co_3O_4 (72.3 mV dec^{-1}), implying a boosted intrinsic activity by oxygen vacancies. Plasma engraving was also employed to create oxygen vacancies into metal oxide catalysts. For example, Wang and co-workers reported that Ar radiofrequency plasma treatment can generate oxygen vacancies in Co_3O_4 nanosheets.¹⁵¹ After plasma treatment, the Co_3O_4 nanosheets possessed rough and discontinuous surfaces, resulting in larger active surface areas. Defect states within the band gaps of Co_3O_4 were detected by DFT calculation, confirming the high electrical conductivity. Owing to the optimized electronic structure and conductivity, the Ar-plasma engraved Co_3O_4 nanosheets exhibited better OER performances than pure Co_3O_4 . These experimental and

theoretical results confirmed that oxygen vacancies are of great significance in improving water splitting performances of TM-based electrocatalysts through the following aspects: (1) work as active centers and increase the density of catalytic site; (2) improve their conductivity by the generation of new gap states or narrow the band gap; and (3) optimize the adsorption/desorption ability of regent species and lower the reaction barriers.¹⁵²⁻¹⁵⁵ Therefore, it is desired to develop additional facile strategies and implement these strategies to precisely engineer the density and distribution of oxygen vacancies in metal oxides-based electrocatalysts to dramatically boost their catalytic performances.

3.5.2. Engineering by cation vacancy defects

As another kind of classical defects, cation vacancy could effectively regulate the surface electronic properties of host catalysts, increase their active sites, and accelerate charge transfer, further promote the reaction kinetics, and reduce the reaction barriers. Compared with oxygen vacancy, metal cation vacancy possesses higher formation energy, but with the rapid improvement of advanced characterization and synthetic technology, engineering the catalytic performances via cation vacancy for efficiently catalyzing HER or OER has attracted attention.^{156,157} For instance, Chen and his co-workers synthesized a nanocrystalline $\text{Co}_x\text{Mn}_{3-x}\text{O}_4$ catalyst with abundant metal (Co or Mn) cation vacancies.¹⁵⁸ DFT calculations revealed that this spinel $\text{Co}_x\text{Mn}_{3-x}\text{O}_4$ catalyst with metal cation vacancies exhibited optimized electronic states, leading to favorable oxygen-binding abilities. Experiment results showed that the as-prepared $\text{Co}_x\text{Mn}_{3-x}\text{O}_4$ catalyst possessed superior catalytic activities toward the OER. Messinger and co-workers reported that Fe vacancies could be introduced into FeP by chemical leaching of Mg and as-obtained Fe vacancy-rich FeP nanoparticulate exhibited superior HER performances to FeP and Mg-doped FeP, possessing η_{10} of 65 mV in 0.5 M H_2SO_4 . The theoretical and experimental analyses demonstrated that Fe vacancies could regulate electronic structures, optimize hydrogen adsorption, as well as contribute to proton trapping, dramatically improving HER activities.¹⁵⁹ Besides, ultrathin ferroxhyte (δ -

FeOOH) nanosheets with Fe vacancies-defect were designed and the optimized structure of δ -FeOOH is shown in Figure 12a.¹⁶⁰ Figure 12b and 12c show the HER and OER performances of defective δ -FeOOH and reference samples in 1 M KOH solution, which clearly demonstrated the enhanced water splitting performances of Fe vacancies-defect δ -FeOOH and theoretical results confirmed that active sites are neighboring Fe atoms to Fe vacancies. In addition, cobalt-defected $\text{Co}_{3-x}\text{O}_4$ as OER catalysts was *in situ* prepared by Zou and co-workers.¹⁶¹ The generation of Co vacancies and distortion structures of prepared $\text{Co}_{3-x}\text{O}_4$ were characterized by XAFS and positron annihilation lifetime spectra (PALS), and the tuned electronic structures of Co-defected $\text{Co}_{3-x}\text{O}_4$ were studied by DFT. As shown in Figure 12d, the $\text{Co}_{3-x}\text{O}_4$ possessed an increased DOS for the occupied states from 0.50 eV above the Fermi level and a smaller bandgap with respect to Co_3O_4 . The presence of Co vacancies could result in distortion to neighboring atoms and electronic delocalization, which are beneficial for faster charge transport during water splitting reactions. Figure 12e displays the process of H_2O adsorption on Co_3O_4 and $\text{Co}_{3-x}\text{O}_4$ surfaces. The hydrogen atom of H_2O molecule was drawn to surface oxygen nearby adsorbed Co site on $\text{Co}_{3-x}\text{O}_4$, and the adsorbed energy of H_2O is -1.07 eV, lower than that on normal Co_3O_4 (-0.98 eV), suggesting Co vacancies could contribute to H_2O adsorption during OER process. As predicted, remarkably high OER performances were obtained with the cobalt-defected $\text{Co}_{3-x}\text{O}_4$ as electrocatalysts (Figure 12f), which deliver a lower η_{10} of 268 mV than normal Co_3O_4 (376 mV) in 1 M KOH solution. Additionally, Liu and co-workers proposed metal-vacancy-solid-solution NiAlP, which could be employed as bifunctional electrocatalysts for all-pH HER and OER.¹⁶² The EDS, ICP, XPS and HRTEM image (Figure 12g) confirmed the formation of Al vacancies in NiAlP after alkali-etching treatment. Figure 12h displays the NiAlP nanowall array with abundant Al vacancies possessed much higher HER performances with a low η_{10} of 35 mV. However, an overpotential of 78 mV is needed to achieve 10 mA cm^{-2} over NiAlP, confirming the enhanced intrinsic HER activity of the defective NiAlP was originated from Al vacancies. In addition, the NiAlP nanowall array with abundant Al vacancies exhibited a smaller Tafel slope of 38 mV dec^{-1} , that

is very close to commercial Pt/C (30 mV dec^{-1}) and superior to NiAlP (89 mV dec^{-1}). Similarly, improved OER performances were also obtained when using Al vacancies-defect NiAlP as the catalyst as shown in Figure 12i, where a lower η_{10} of 256 mV and a smaller Tafel slope of 76 mV dec^{-1} were obtained, which are much better than NiAlP sample without vacancies. Moreover, the as-prepared Al-vacancies defect-rich NiAlP nanowall arrays exhibited outstanding water splitting activities, needing low cell voltages of 1.50–1.70 V to reach 10 mA cm^{-2} under pH of 0–14. Furthermore, the calculated band structure of NiAlP with Al vacancies (Figure 12j) displays high charge densities distributed around the Fermi level, which is greater than that of perfect NiAlP, suggesting that the introduced Al-vacancies sped up the electron transfer during reactions. The partial charge density (Figure 12k) shows that Al vacancies could enhance the electrons delocalization, leading to more efficient centers toward water electrocatalysis. The ΔG_{H^*} and H_2O adsorption energy plots (Figure 12l) indicated that the surface with Al vacancies is beneficial to proton and O-related species adsorption. The results manifested that well-designed metal vacancies in electrocatalysts could optimize the electronic properties and provide more active centers, thus endowing catalysts with excellent activities toward both HER and OER. Accordingly, it is crucial to design facile methods to create cation vacancies into TM-based electrocatalysts and make efforts to explore the relationship between cation vacancies and electronic structures.¹⁶³⁻¹⁶⁶

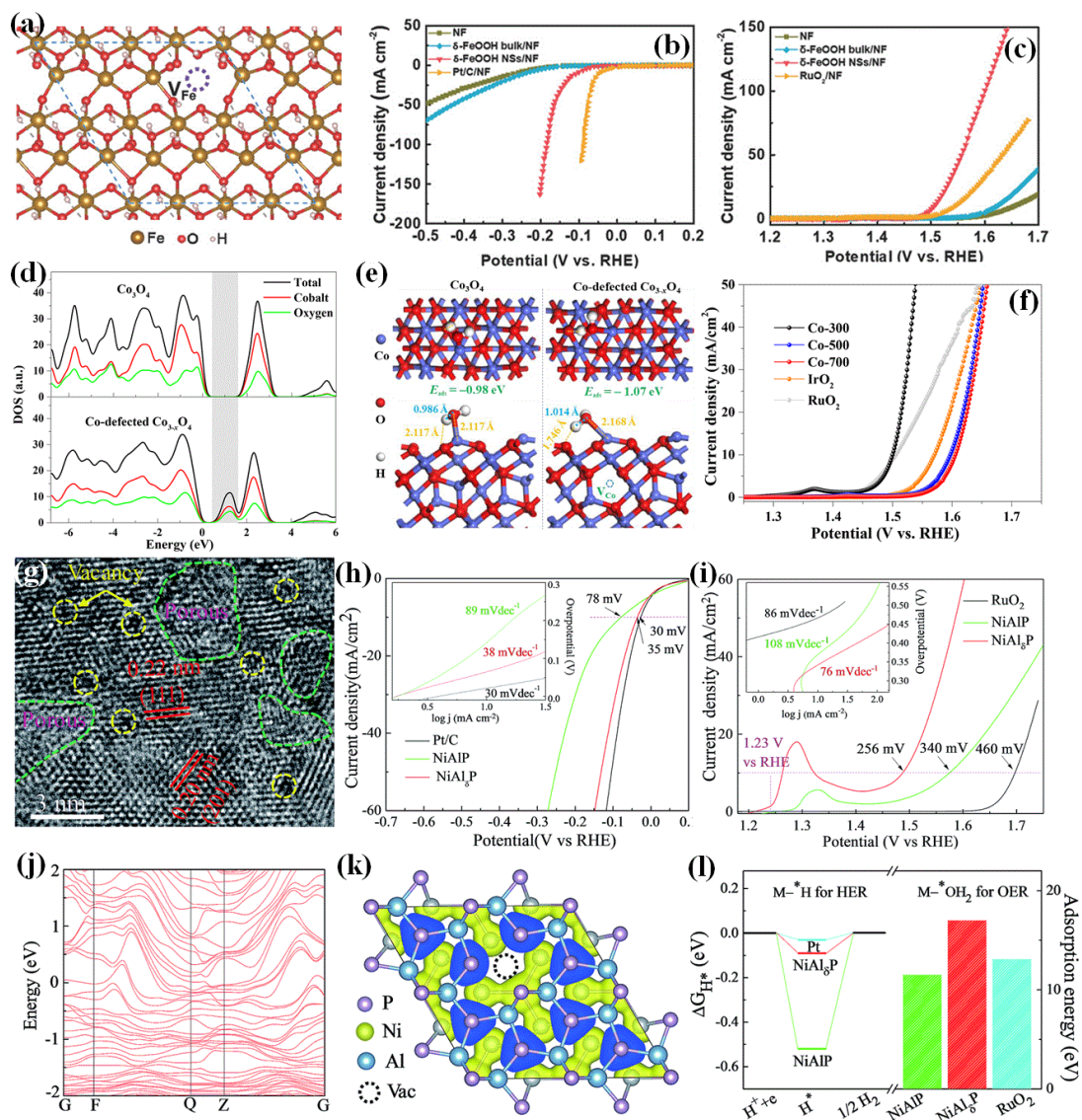


Figure 12. (a) The optimized structure of δ -FeOOH with Fe vacancy. (b) The LSV curves for HER and (c) LSV curves for OER in 1.0 M KOH electrolyte. Reproduced with permission.¹⁶⁰ Copyright 2018, Wiley-VCH. (d) Calculated total and projected DOS of Co₃O₄ and Co-defected Co_{3-x}O₄. (e) Optimized configurations of H₂O adsorbed on (111) surface of Co₃O₄ (top and side views, (left) and Co-defected Co_{3-x}O₄ (right). (f) LSV curves for OER of Co_{3-x}O₄ samples calcined at 300, 400 and 500 °C (denoted as Co-300, Co-500, Co-700), IrO₂ and RuO₂ samples in 1 M KOH solution. Reproduced with permission.¹⁶¹ Copyright 2018, American Chemical Society. (g) HRTEM image of obtained NiAlP with Al vacancies. (h) The HER and (i) OER performances of NiAlP nanowall array with/without Al vacancies. Insets: the corresponding Tafel plots. (j) The

calculated band structure of NiAlP with Al vacancies. (k) The local charge density of NiAlP with Al vacancies. (l) The calculated ΔG_{H^*} diagram and H₂O adsorption energy values over NiAlP, NiAl_{1-x}P_x with Al vacancies and Pt or RuO₂. Reproduced with permission.¹⁶² Copyright 2018, Royal Society of Chemistry.

3.5.3. Engineering by multi-vacancies defects

As mentioned above, both anion and cation vacancy can efficiently engineer the electronic structures of TM-based materials to improve their electrocatalytic performances. Therefore, introducing multi-vacancies with different types into nanomaterials could also be a promising strategy to greatly tune their electrocatalytic activities. For example, Fan and co-workers reported fluorine could induce dual defects (F-anion doping and P vacancy) into cobalt phosphide nanosheets and then the dual defects can greatly boost the electrocatalytic performances.¹⁶⁷ The successful formation of dual defects in CoP nanosheets was proved by in situ depth XPS and EXAFS spectra. In Figure 13a, peaks with binding energies of 782.3 eV and 798.4 eV are ascribed to Co²⁺, which is generated from the ionic Co²⁺-F and Co²⁺-O bonds. The F 1s spectrum (Figure 13b) also confirms the appearance of F-Co bonds (peak at 685.5 eV), which clearly proves the successful introduction of F atoms into the CoP nanosheets. In Figure 13c, the absorption edge of CoP with F doping and P vacancy (denoted as F-CoP-V_p) located at a higher energy than pure CoP, confirming an increased valence state of Co in F-CoP-V_p due to the electronegative F atoms incorporation. In addition, the corresponding fitting curves confirm the formation of P vacancies in F-CoP-V_p sample. DFT calculation revealed that the F doping could result in easier adsorption of water molecular and P vacancies could make the ΔG_{H^*} reduced closer to zero (Figure 13d). Meanwhile, the obtained charge density distribution revealed that F doping can trigger localization of charge density distribution and further increase electrical conductivity. As a result, the dual defects lead to nearly 15-fold enhancement toward experimentally catalytic HER in neutral media (Figure 13f). Wang and co-workers presented a simple

approach (Figure 13g) to introduce multiple vacancies (Co, Fe and O vacancies) into 2D CoFe LDHs (denoted as E-CoFe LDHs) by acid-base reaction, which finally led to significantly enhanced OER performances.¹⁶⁸ To prove the successful generation of multi vacancies defects and investigate the tuned electronic structures by multi vacancies, XAS was employed. Figure 13h and 13i shows coordination environment changes of Co and Fe atom caused by defects. The Fourier transform (FT) of EXAFS curves for Co K-edge (Figure 13j and 13k) displays Fe-O and Fe-Co coordination peaks largely decreased after acid etching, confirming the appearance of oxygen vacancies and iron vacancies. Figure 13l shows the catalytic LSV curves, where the E-CoFe LDHs with multi vacancies defects exhibited higher OER performances than perfect CoFe LDHs. Besides, Ar plasma etching was employed to convert the bulk CoFe LDHs into monolayer nanosheets, and abundant Co, Fe, and O vacancies were created at the same time.¹⁶⁹ These introduced multi vacancies defects (O, Co, and Fe vacancies) led to more exposed active sites and dramatically enhanced their intrinsic electrocatalytic activities of 2D CoFe LDHs nanosheets. Similarly, a water-plasma-enabled exfoliation method was also employed to introduce O, Co, and Fe vacancies into CoFe LDH for water oxidation.¹⁷⁰ Moreover, Cai and co-workers presented an efficient neutral water electrolyzer material based on LDH with O, Ni, and Fe multiple vacancy defects. Because of these multiple vacancy defects, the prepared NiFe LDH possessing improved electrical conductivity and faster charge transfer, displayed a small η_{10} of 87 mV for HER in a pH 7 buffer electrolyte.¹⁷¹

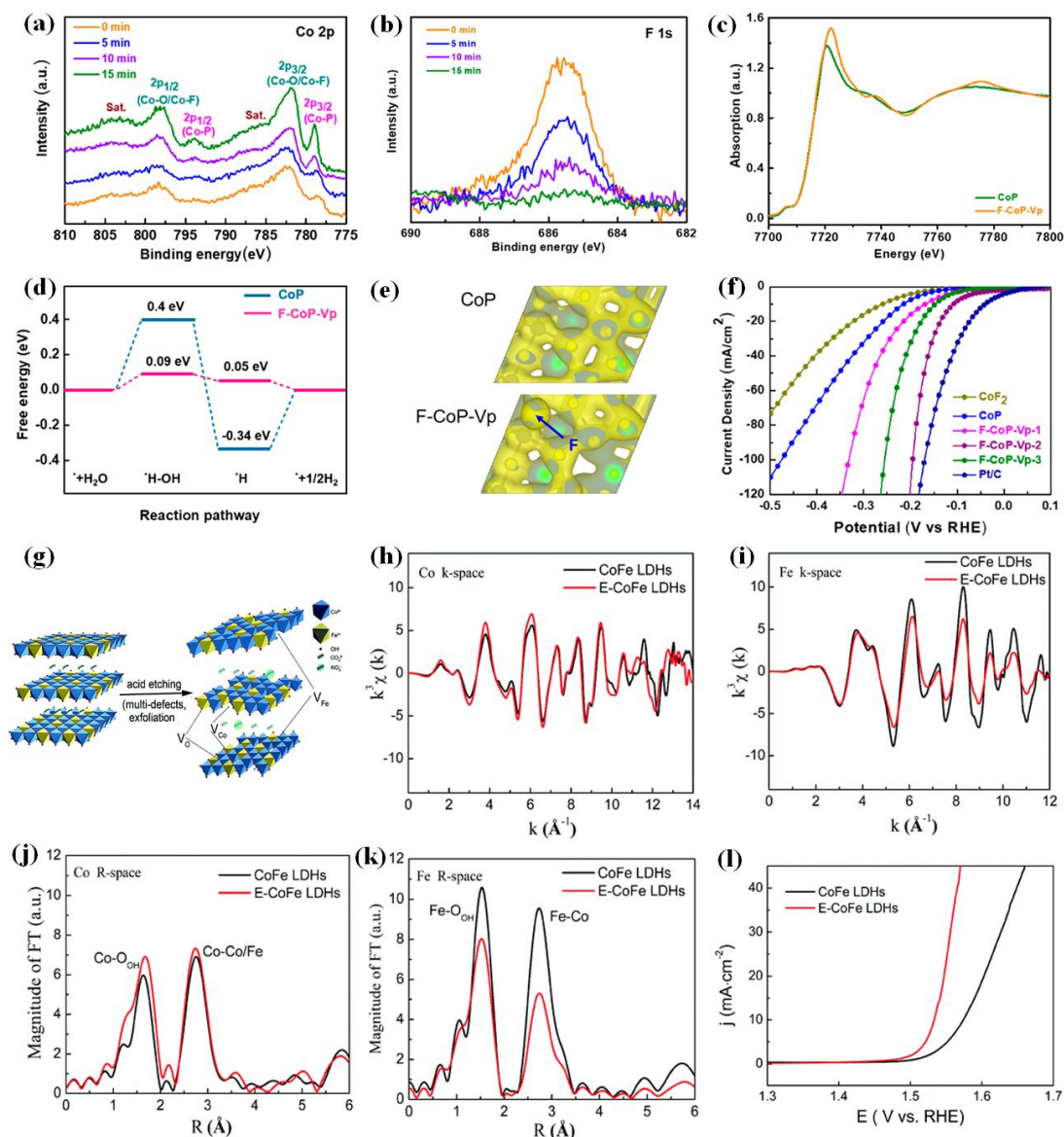


Figure 13. The in situ depth Co 2p (a) and F 1s (b) XPS patterns in F-CoP-V_{p-2} nanosheets. (c) Co K-edge XANES spectra of the F-CoP-V_{p-2} nanosheets. (d) Reaction pathways of HER over the (211) surfaces of CoP and F-CoP-V_p. (e) Charge density distribution of CoP (top) and F-CoP-V_p (bottom). (f) The LSV curves for HER of commercial Pt/C, CoF₂, CoP and F-CoP-V_p samples in 1 M PBS electrolyte. Reproduced with permission.¹⁶⁷ Copyright 2020, American Chemical Society. (g) The process of synthesizing CoFe LDHs with O, Co and Fe multi-vacancies. (h) Co and (i) Fe K-edge extended XANES oscillation functions $k^3\chi(k)$ of FeCo LDHs and E-FeCo LDHs with multi-vacancies. (j) Co and (k) Fe K-edge Fourier transform magnitudes of EXAFS. (l) LSV curves of FeCo LDHs and E-FeCo LDHs for OER in the alkaline

electrolyte. Reproduced with permission.¹⁶⁸ Copyright 2017, Royal Society of Chemistry.

3.6. Other strategies for engineering electrocatalysts

Besides aforementioned strategies, some others have also been employed to engineer the electronic structures of TM-based materials to further enhance their electrocatalytic performances. Varying the particle size of catalysts could regulate their electronic structures and lead to more active centers. For example, Behm and co-workers explored the dependence of HER performances on the Pt NC sizes. A volcano-like relationship between activities and sizes was obtained, and Pt NCs with ca. 38 atoms displayed highest j_0 .¹⁷² Zeng and co-workers designed a facile approach to boost the OER performances of perovskite cobaltite LaCoO₃ through reducing the particle size.¹⁷³ Tuning the sizes of LaCoO₃ could efficiently engineer their e_g filling, leading to the transform from low-spin to high-spin states of Co ions and more active sites at the surfaces. When the average sizes of LaCoO₃ particles were reduced to approximately 80 nm, e_g filling of Co reached to optimal value of 1.2 and their OER performances were dramatically enhanced compared with LaCoO₃ bulks. Moreover, when the size of catalysts decreased to single atom level, the utilization efficiency of metal centers and the number of exposed active sites can be significantly changed, consequently regulating the electrocatalytic activities. For example, Allen J. Bard and co-workers investigated the size effects on the HER using the single-Pt atoms, Pt clusters, and Pt NPs as examples, where the HER kinetics increased with size increasing (0.2 ~ 4 nm) and reached the limitation of activity.¹⁷⁴ Wang and co-workers synthesized single-atom Pt anchored onto N-doped porous carbon with Pt loading of 3.8 wt% via a photochemical solid-phase reduction approach.¹⁷⁵ As-prepared Pt₁/NPC catalyst exhibited ultrahigh electrocatalytic performances toward HER with a low η_{10} of 25 mV and its mass activity was 24-times better than Pt/C catalyst.

The lattice tensile strain could also be useful to regulate electronic structures of TM-based catalysts and boost their electrocatalytic performances. For example, Guo et al.

presented that Co₉S₈/MoS₂ core/shell nanocrystals with precisely tuned tensile surface strain exhibited greatly boosted HER activities. The tensile strain of Co₉S₈/MoS₂ can change from 3.5% to 0% through tuning shell layers of MoS₂ and the Co₉S₈/MoS₂ sample with tensile strain of 3.5% displayed the best HER performances.¹⁷⁶ DFT calculation confirmed that the optimal Co₉S₈/MoS₂ nanostructure possessed the lowest reaction barrier of 0.29 eV and H adsorption energy of -1.03 eV due to the lattice tensile strain effects. Li and his co-workers employed the compressive strain to construct IrO_x layers on IrCo nanodendrites.¹⁷⁷ In situ EXAFS showed that its compressive strain could be tuned from 2.51% to unstrained state, which further led to variations in electrocatalytic OER activities. DFT calculations showed that the optimized strain can optimize the adsorption ability and promote the generation of HOO* species. Experimental results revealed that IrO_x with three layers on IrCo (approximately 1.51% strain), showed the best OER performances with a small η_{10} of only 247 mV in acid solution. Furthermore, Liu and co-workers reported that lattice tensile strain could engineer the anti-bonding filling states of the d orbital in NiFe hydroxide and boost oxygenated intermediates adsorption, thus dramatically boosting the water oxidation performances.¹⁷⁸ Moreover, Liu et al. reported that lattice-strained NiFe metal-organic frameworks (MOFs) showed much better activities than pristine NiFe MOFs.¹⁷⁹ Therefore, engineering the lattice tensile strain is a facile and potential strategy to regulate their electronic structures and optimize their adsorption abilities of TM-based catalysts for efficient electrocatalysis.

Controlling the coordination structure can also regulate the electron densities around TM sites, enhance electronic conductivity, and increase the exposed active sites of catalysts. For example, Xie and her co-workers revealed that coordination number of Co ions can be reduced from 5 to 3 by introducing pores in the surfaces of Co₃O₄ nanosheets.¹⁸⁰ The Co³⁺ sites could work as chemically catalytic OER centers and enhance conductivity through increasing DOS at the band edge. Consequently, the as-prepared porous Co₃O₄ atomically thick sheets displayed an electrocatalytic OER current density of 341.7 mA cm⁻² at 1.0 V, approximately 50-times higher than Co₃O₄

bulks. Afterward, a heterostructure electrocatalyst containing low-coordinate IrO₂ confined on graphitic carbon nitride (GCN) was reported.¹⁸¹ The coordination number of Ir atoms could result in lattice strain, further increase the electron densities around Ir sites, and optimize the adsorption ability of intermediates over the surfaces, thus greatly boosting the electrocatalytic performances. Besides, Fei et al. reported that Co–N linkage in Co–N–C catalyst could contribute to better performances towards HER.¹⁸² Cao et al. synthesized Co-based HER catalyst by embedding Co atoms into P-doped g-C₃N₄, which exhibited a η_{10} of 89 mV in 1 M KOH.¹⁸³ In addition, Sa et al. synthesized HER catalysts with Co–N_x moieties supported onto CNT, in which the coordination structure of pyridine-type Co–N₄ showed best performance.¹⁸⁴ Consequently, controlling the coordination structure of TM-based electrocatalyst could be another effective strategy for engineering their electronic structures and greatly booting their electrocatalytic activities.

Table 2. Summary of the strategies used to enhance catalytic activities of TM-based electrocatalysts.

Strategies	Catalysts	Reaction	Electrolyte	η_{10} (mV)	Tafel Slope (mV dec ⁻¹)	Reference
Support Effects	Mo ₂ C@NPC	HER	0.5 M H ₂ SO ₄	260	126.4	<i>Nat. Commun.</i> 2016 , 7, 11204.
	Mo ₂ C@NPC/NPRGO			34	33.6	
	FeCo alloy in Graphene Layer	HER	1.0 M KOH	149	77	<i>ACS Catal.</i> 2017 , 7, 469.
	RuCo@NC	HER	1.0 M KOH	28	31	<i>Nat. Commun.</i> 2017 , 8, 14969.
	Pure CoSe ₂	OER	0.1 M KOH	484	66	<i>ACS Nano</i> 2014 , 8, 3970.
	NG-CoSe ₂			366	40	
	Co ₃ (PO ₄) ₂	OER	1.0 M KOH	-	103	<i>J. Mater. Chem. A</i> 2016 , 4, 8155.
	Co ₃ (PO ₄) ₂ @N-C			317	62	
	FeOOH	OER	1.0 M KOH	-	101	<i>Adv. Energy Mater.</i> 2018 , 8, 1702598.
FeOOH/NPC	-			33.8		

Interface Effects	Ni ₃ N/Ni/NF	HER	1.0 M KPi	19	-	<i>Nat. Commun.</i> 2018 , 9, 4531.
			1.0 M KOH	12	29.3	
	GC/TaS ₂	HER	0.5 M H ₂ SO ₄	267	89	<i>ACS Nano</i> 2019 , 13, 11874.
	CF/TaS ₂			186	73	
	Mo/TaS ₂			110	58	
	Au/TaS ₂			101	53	
	W _x C@WS ₂ -10	HER	0.5 M H ₂ SO ₄	156	75	<i>Adv. Funct. Mater.</i> 2017 , 27, 1605802.
	W _x C-60			192	68	
	WS ₂			318.7	110	
	W ₂ N/WC	OER	1.0 M KOH	320	94.5	<i>Adv. Mater.</i> 2020 , 32, 1905679.
Crystal Faces	Ni ₃ S ₂ /NF	HER	1.0 M KOH	223	-	<i>J. Am. Chem. Soc.</i> 2015 , 137, 14023.
		OER		260	-	
	Co ₃ O ₄ -NC/N-rGO	OER	1.0 M KOH	440	124	<i>Adv. Energy Mater.</i> 2018 , 8, 1702222.
	Co ₃ O ₄ -NTO/N-rGO			410	78	
	Co ₃ O ₄ -NP/N-rGO			380	62	
	{110} faces exposed Co ₃ O ₄ nanosheets	OER	1.0 M KOH	318	66	<i>ACS Appl. Mater. Interfaces</i> 2018 , 10, 7079.
	{111} faces exposed Co ₃ O ₄ nanosheets			339	69.4	
	{112} faces exposed Co ₃ O ₄ nanosheets			320	57.6	
	Bulk TaC	HER	0.5 M H ₂ SO ₄	> 400	232	<i>Nano Energy</i> 2017 , 36, 374.
	TaC NCs@C			146	143	
Elemental Doping	CC@CoP	HER	0.5 M H ₂ SO ₄	85	50.5	<i>Adv. Mater.</i> 2018 , 30, 1800140.
	CC@N-CoP			42	41.2	
	Cu ₇ S ₄	OER	1.0 M KOH	510	197	<i>ACS Nano</i> 2017 , 11,

	Co-Cu ₇ S ₄ -0.07			270	130	12230.
	Co-MoS ₂ /BCCF-21	HER	1.0 M KOH	48	52	<i>Adv. Mater.</i> 2018 , <i>30</i> , 1801450.
		OER		260	85	
	VS ₂ /CP	HER	0.5 M H ₂ SO ₄	257	125.87	<i>ACS Nano</i> 2020 , <i>14</i> , 5600.
	1Pt/VS ₂ /CP			77	40.13	
	MoS ₂	HER	0.5 M H ₂ SO ₄	328	157	<i>Nat. Commun.</i> 2018 , <i>9</i> , 2120.
	1% Pd-MoS ₂ /CP			89	32	
	Ni(OH) ₂ -r	OER	1.0 M KOH	351	111	<i>Nat. Commun.</i> 2019 , <i>10</i> , 2149.
	w-Ni(OH) ₂ -e			264	58	
	w-Ni(OH) ₂ -e			237	33	
	Co ₄ N	HER	1.0 M KOH	150	128	<i>Adv. Energy Mater.</i> 2019 , <i>9</i> , 1902449.
	Cr-Co ₄ N			21	38.1	
Defects	WO _{3-p} NSs	HER	0.5 M H ₂ SO ₄	245	78	<i>Nano Lett.</i> 2017 , <i>17</i> , 7968.
	WO _{3-r} NSs			38	38	
	Pristine Co ₃ O ₄	OER	1.0 M KOH	-	82	<i>Adv. Energy Mater.</i> 2014 , <i>4</i> , 1400696.
	Reduced Co ₃ O ₄			-	72	
	P-Co ₃ O ₄	OER	1.0 M KOH	-	72.3	<i>Adv. Energy Mater.</i> 2018 , <i>8</i> , 1701694
	O-Co ₃ O ₄			-	41.9	
	Pristine Co ₃ O ₄	OER	0.1 M KOH	540	234	<i>Angew. Chem., Int. Ed.</i> 2016 , <i>55</i> , 5277.
	plasma engraved Co ₃ O ₄ (120s)			300	68	
	δ -FeOOH NSs/NF	HER	1.0 M KOH	108	68	<i>Adv. Mater.</i> 2018 , <i>30</i> , 1803144
		OER		265	36	
	Co _{3-x} O ₄	OER	1.0 M KOH	268	38.2	<i>ACS Catal.</i> 2018 , <i>8</i> , 3803.

NiAlP	HER	0.5 M H ₂ SO ₄	78	89	<i>J. Mater. Chem. A</i> 2018 , 6, 9420.
	OER		340	108	
NiAl ₅ P	HER		35	38	
	OER		256	76	
CoP	HER	1.0 M PBS	215	123.2	<i>ACS Materials Lett.</i> 2020 , 2, 736.
F-CoP-Vp-2			108	88.9	
CoFe LDHs-Ar	OER	1.0 M KOH	266	37.85	<i>Angew. Chem. Int. Ed.</i> 2017 , 56, 5867.
E-CoFe LDHs	OER	1.0 M KOH	300	41	<i>Chem. Commun.</i> 2017 , 53, 11778.

4. Reaction Mechanisms

Generally, electrocatalytic water splitting occurs at the interfaces between electrocatalysts and electrolyte, which involve the absorption of reactants onto the catalyst surfaces, the migration of intermediate species, and the desorption of produced gases, indicating that the intrinsic electronic structures of the catalysts can determine its electrocatalytic performances.¹⁸⁵⁻¹⁸⁸ Based on the above-detailed discussions about the TM-based electrocatalysts, we drew the corresponding conclusion about the structure–performance relationships that the structures/compositions of materials determine their intrinsic electronic structures, and further alter the reaction mechanisms and catalytic performances. Moreover, these strategies summarized in this review could efficiently engineer the electronic structures of TM-based electrocatalysts to improve their conductivities, increase active sites, optimize adsorption/desorption abilities, and reduce reaction barriers, leading to enhanced performances towards hydrogen or

oxygen evolution reactions. For example, support effects could improve conductivity and accelerate charge transfer by regulating electronic structures of active materials, further greatly improving the electrocatalytic performances. Interface effects and crystal face tuning strategies could increase the active sites and regulate the intrinsic sites by engineering their electronic structures, leading to enhanced catalytic performances. Elemental doping and defects tuning strategies could improve the conductivity, increase the active site densities, optimize the adsorption of reactant species, and reduce the related reaction barriers by regulating the electronic structures of TM-based catalysts. Consequently, it is imperative to deeply explore the mechanism of water splitting reactions and carefully analyze the relationship between structures and performances of TM-based electrocatalysts.

Recently, operando analysis has been employed as useful methods for providing profound insights into the underlying reaction mechanisms.¹⁸⁹⁻¹⁹⁴ For example, Liu et al. utilized in situ XANES and EXAFS to study active sites and the dynamic variation of electronic configuration over hierarchical binary Ni–Co oxide catalyst during water oxidation.¹⁹⁵ The generation of NiOOH was demonstrated by in situ EXAFS spectra and the oxidation of Ni during OER was confirmed by operando EXAFS spectra, suggesting NiOOH worked as active site. Wang et al. explored the nature of high OER performances of state-of-the-art multi-metal oxides/(oxy)hydroxides at the atomic level using in-situ XAS.¹⁹⁶ A short V-O bond was detected during OER by in-situ X-ray absorption spectroscopic, suggesting V atoms can greatly contribute to the OER activity. Moreover, Schmidt and co-workers decoupled the activity losses towards high surface

area iridium oxides using operando X-ray characterization, making it possible to expound degradation mechanisms of OER.¹⁹⁷

5. Conclusions and outlook

In this review paper, previously reported strategies of engineering TM-based catalysts to improve their electrocatalytic oxygen or hydrogen evolution activities were summarized and shown in Figure 14, which are crucial in ameliorating global energy and environmental issues. These strategies including support effects, interface effects, crystal face tuning, elemental doping, and defect tuning could remarkably regulate the electronic structures of TM-based nanomaterials and enhance their electrocatalytic activities as shown in Table 2. Nonetheless, developing facile methods of engineering various TM-based catalysts for excellent electrochemical H₂ production to replace the fossil fuels and deeply understanding the catalytic mechanism are still at an immature stage. Several aspects that further attention should be devoted to are listed below.

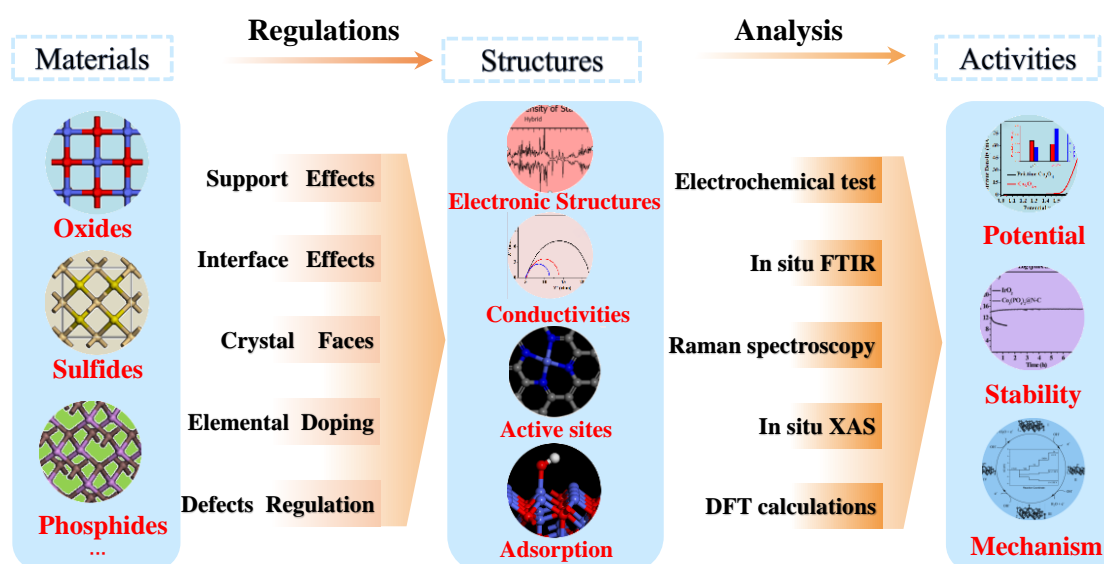


Figure 14. Perspective: potential strategies of engineering transition metal-based materials for H₂ production via water splitting.

(I) Currently, various TM-based materials with different intrinsic electronic

structures have been prepared as powerful electrocatalysts for HER and OER, however, ideal catalysts are still yet to be realized to replace commercial noble metal catalysts.¹⁹⁸⁻²⁰⁵ Thus, fundamentally designing novel TM-based materials with fine electronic structures and deeply understanding their electronic structure–property relationships need to be intensively explored.

(II) The mentioned strategies of engineering electrocatalysts in this review paper could work as useful methods in engineering the intrinsic electronic structures and boosting the catalytic performances of TM-based electrocatalysts. Therefore, these strategies should be continuously focused on until ideal electrocatalysts with excellent catalytic performances and stabilities are realized. Moreover, other effective and novel strategies, such as electric or magnetic fields tuning, electrolyte tuning, are also expected to greatly engineer electrocatalysts, further dramatically boosting their catalytic water splitting activity.

(III) The in-depth fundamental studies of regulated electronic structures, active centers and tuned catalytic activities need to be intensively explored using advanced characterization methods or in situ testing techniques or DFT calculations to understanding the structure-property relationship. The obtained structure–property relationship can be used to provide scientific guidance for optimizing the electrocatalysts. Advanced techniques such as in situ Raman spectroscopy, Fourier Transform Infrared Spectrometer (FTIR), X-ray absorption spectroscopy (XAS), and Molecular Dynamics simulation, as well as experimental techniques combined with computational simulations should be employed to propose deep insights into the electronic structures.

(IV) Pushing the low-cost and efficient electrocatalysts into large-scale industrial application even at harsh electrolyte conditions or very high/low potentials must be considered. The currently reported electrocatalysts were usually tested in the laboratory under mild condition, and the long-term stability is insufficient. Thus, designing or engineering the catalysts to make them more active and preserve these active sites at extreme electrolyte or potential conditions for clean energy generation at a much larger

scale is urgent and requires further research.

Notes

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TOC Figure

